Catalyst support, process for its preparation and use

The present invention relates to an open-pore catalyst support consisting of a material which comprises a natural sheet silicate and ZrO_2.

Alkenyl acetates are an important monomer building block in the synthesis of plastic polymers. The main fields of use of alkenyl acetates are i.a. the preparation of polyvinyl acetate, polyvinyl alcohol and polyvinyl acetal and also co- and terpolymerization with other monomers such as for example ethylene, vinyl chloride, acrylate, maleinate, fumarate and vinyl laurate.

Alkenyl acetates are prepared for example in the gas phase from acetic acid and ethylene by reaction with oxygen, wherein the catalysts used for this synthesis preferably contain Pd as active metal, Au as promoter and an alkali metal component as co-promoter, preferably potassium in the form of the acetate. In the Pd/Au system of these catalysts, the metals Pd and Au are not present in the form of metal particles of the respective pure metal, but rather in the form of Pd/Au-alloy particles of possibly different composition, although the presence of unalloyed particles cannot be ruled out. As an alternative to Au, for example Cd or Ba can also be used as co-promoter.

Currently, alkenyl acetates are predominantly prepared by means of so-called shell catalysts in which the noble metals Pd and Au do not fully penetrate the catalyst support formed as a shaped body, but rather are contained only in an outer area (shell) of greater or lesser width of the catalyst

support shaped body (cf. on this EP 565 952 A1, EP 634 214 A1, EP 634 209 A1 and EP 634 208 A1), while the areas of the catalyst support lying further inside are free of noble metals. With the help of shell catalysts, a more selective reaction control is possible in many cases than with catalysts in which the supports are impregnated into the core of the support with active component ("impregnated through").

The shell catalysts known in the state of the art for the preparation of alkenyl acetates can be for example catalyst supports based on silicon oxide, aluminium oxide, aluminosilicate, titanium oxide or zirconium oxide (cf. on this EP 839 793 A1, WO 1998/018553 A1, WO 2000/058008 A1 and WO 2005/061107 A1). Catalyst supports based on titanium oxide or zirconium oxide are currently scarcely used, however, since these catalyst supports display no long-term resistance to acetic acid and are relatively expensive. In the case of shell catalysts coated with Zr suspension, problems with the abrasion resistance and mechanical stability arise.

The great majority of the catalysts currently used for the preparation of alkenyl acetates are shell catalysts with a Pd/Au shell on a porous amorphous aluminosilicate support formed as a sphere based on natural sheet silicates which are impregnated through with potassium acetate as co-promoter.

Such alkenyl acetate shell catalysts are usually prepared by the so-called chemical route in which the catalyst support is [steeped in] solutions of corresponding metal precursor compounds, for example by dipping the support into the solutions, or by means of the incipient wetness method (pore-filling method) in which the support is loaded with a volume of solution corresponding to its pore volume.

The Pd/Au shell of the catalyst is produced for example by first steeping the catalyst support in a first step in a Pd salt solution and then in a second step fixing the Pd component with a base, e.g. NaOH, onto the catalyst support in the form of a Pd-hydroxide compound. In a subsequent, separate third step, the catalyst support is then steeped in an Au-salt solution and then the Au component is likewise fixed by means of a base. After the fixing of the noble-metal components in the outer shell of the catalyst support, the support is washed, then dried, optionally calcined and finally reduced. The thus-produced Pd/Au shell is usually approximately 100 µm to 500 µm thick.

Usually, the catalyst support loaded with the noble metals is loaded with potassium acetate after the last fixing or reducing step wherein, rather than the loading with potassium acetate taking place only in the outer shell loaded with noble metals, the catalyst support is completely impregnated through with the co-promoter. A spherical support called "KA-160" from SÜD-Chemie AG, Munich, Germany, based on a natural sheet silicate, which has a BET surface area of approximately 160 m^2/g, is predominantly used as catalyst support.

The alkenyl acetate selectivities achieved by means of the shell catalysts known in the state of the art based on Pd and Au and also KA-160 supports are approximately 90 mol-%, relative to the supplied ethylene, wherein the remaining 10 mol-% of the reaction products are essentially CO_2 which is formed by total oxidation of the organic educts/products.

To increase the activity of alkenyl acetate catalysts, before the deposition of the noble metal, catalyst supports free of active metal, based on natural sheet silicates, are first surface-doped with zirconium cations. For this, for example

ready-formed catalyst support shaped bodies are impregnated with a solution of a zirconium salt compound and then calcined. Although, compared with the corresponding catalysts without zirconium doping, such catalysts are characterized by increased activity with respect to alkenyl acetate production, the increased activity is not of long duration, as because of the corrosive atmosphere in alkenyl acetate synthesis the Zr is released relatively rapidly from the catalyst support and is therefore no longer available for activation of the catalyst. The zirconium applied by impregnation is not sufficiently resistant to acetic acid under process conditions even after the calcining of a modified support.

The object of the present invention is therefore to provide a catalyst support, by means of which alkenyl acetate catalysts can be prepared which are characterized by a relatively high level of alkenyl acetate activity over a relatively long period.

This object is achieved by a first open-pore catalyst support consisting of a material which comprises a natural sheet silicate and ZrO_2 in the tetragonal modification.

Surprisingly, it was discovered that, by means of an open-pore catalyst support consisting of a material which comprises a natural sheet silicate and ZrO_2, wherein the ZrO_2 is present in the tetragonal modification, alkenyl acetate catalysts can be prepared, which are characterized by a relatively high level of alkenyl acetate activity over a relatively long period.

ZrO_2 occurs in three modifications. ZrO_2 is present in the monoclinic modification at room temperature, in the tetragonal modification at a temperature above 1170°C and in the cubic modification above 2370°C up to the melting point at 2690°C.

In the catalyst support according to the invention the high-temperature tetragonal modification of the ZrO_2 is stable at room temperature.

According to a preferred embodiment of the first catalyst support according to the invention it is provided that the catalyst support in boiling acetic acid releases less than 0.06 wt.-% Zr calculated as ZrO_2, relative to the weight of the ZrO_2 contained in the catalyst support.

It was found that the solubility in acetic acid of the ZrO_2 contained in the first catalyst support according to the invention is relatively low and the catalyst support therefore loses little ZrO_2, with the result that relatively little ZrO_2 needs to be contained in the catalyst support in order to maintain the increased activity of a corresponding catalyst over a relatively long period. It was also possible to show that by means of the process according to the invention for the preparation of the catalyst support according to the invention, supports can be obtained which have ZrO_2 which is only 0.05 wt.-% to 0.0001 wt.-% soluble in boiling acetic acid, relative to the weight of the ZrO_2 contained in the catalyst support. Accordingly, according to a preferred embodiment of the first catalyst support according to the invention, it is provided that the catalyst support releases less than 0.06 wt.-% Zr in boiling acetic acid calculated as ZrO_2, relative to the weight of the ZrO_2 contained in the catalyst support, preferably 0.05 wt.-% to 0.0001 wt.-%, more preferably 0.01 wt.-% to 0.0003 wt.-%, still more preferably 0.008 wt.-% to 0.0005 wt.-% and further preferably 0.003 wt.-% to 0.0008 wt.-%.

In order to determine the Zr release of the catalyst support according to the invention 10 g of the dry catalyst support in powder form is boiled in 250 ml of 96% boiling acetic acid (pro analysi) for 1 h at normal pressure under reflux conditions. The catalyst support is then separated via a filter, the filtrate evaporated until dry and the mass of the remaining solid residue determined. This residue, by comparison with the quantity of catalyst support used, provides information on how soluble the catalyst support is in acetic acid. The zirconium content of the solid residue is determined by means of *Inductively Coupled Plasma* (ICP) and from this the quantity of Zr released from the catalyst support is calculated as ZrO_2. It is assumed that all the zirconium contained in the support is present as zirconium dioxide. The quantities of sample and agents used for determining the support's solubility in acetic acid can if required be scaled up, in each case by the same factor, in order to achieve greater accuracy.

The total zirconium content of the catalyst support is determined by means of suitable information and ICP-analysis and from this the total zirconium dioxide content of the support is calculated. It is assumed that all the zirconium contained in the support is present as zirconium dioxide. The Zr release of the catalyst support in boiling acetic acid (calculated as ZrO_2) relative to the total quantity of ZrO_2 contained in the catalyst support is calculated as follows:

Zr release of the catalyst support (calculated as ZrO_2 release) [wt.-%] = (Zr released from the sample (calculated as ZrO_2)[g]/(total zirconium dioxide content of the sample [%] * mass of the catalyst support sample [g]) *100 wt.-%. For example: 10 g of catalyst support with a Zr content of 7.40 wt.-% (corresponding to 10 g of ZrO_2) are treated in acetic

acid. 0.074 g of Zr is detected in the eluate. The Zr release is calculated as (0.074 g*(123.223)/91.224))/10 g = 0.1%.

The present invention further relates to a second catalyst support which achieves the abovementioned object. This second open-pore catalyst support consisting of a material which comprises a natural sheet silicate and ZrO_2, wherein the catalyst support in boiling acetic acid releases less than 0.06 wt.-% Zr calculated as ZrO_2, relative to the weight of the ZrO_2 contained in the catalyst support.

The ZrO_2 contained in the second catalyst support according to the invention has a relatively low solubility in acetic acid, with the result that relatively little ZrO_2 needs to be contained in the catalyst support in order to maintain the increased activity of a corresponding alkenyl acetate catalyst over a relatively long period. It was also possible to show that by means of the process according to the invention for the preparation of the catalyst support according to the invention, supports can be obtained which have ZrO_2 which is only 0.05 wt.-% to 0.0001 wt.-% soluble in boiling acetic acid, relative to the weight of the ZrO_2 contained in the catalyst support. Accordingly it is provided that the second catalyst support according to the invention releases less than 0.06 wt.-% Zr in boiling acetic acid calculated as ZrO_2, relative to the weight of the ZrO_2 contained in the catalyst support, preferably 0.05 wt.-% to 0.0001 wt.-%, more preferably 0.01 wt.-% to 0.0003 wt.-%, still more preferably 0.008 wt.-% to 0.0005 wt.-% and further preferably 0.003 wt.-% to 0.0008 wt.-%. The Zr release in acetic acid is determined as explained above.

The following preferred embodiments of the catalyst support according to the invention relate to both the first and the second catalyst support according to the invention.

According to a preferred embodiment of the catalyst support according to the invention, it is provided that at least 50 wt.-% of the ZrO_2 contained in the catalyst support is present in the tetragonal modification. As the proportion of the ZrO_2 with tetragonal modification contained in the catalyst support according to the invention is determined by means of X-ray diffractometry (XRD), said proportion refers only to X-ray diffraction active ZrO_2 which is contained in the catalyst support according to the invention.

According to the invention it is preferred that at least 50 wt.-% of the ZrO_2 contained in the catalyst support according to the invention is X-ray diffraction active, preferably at least 70 wt.-%, more preferably at least 80 wt.-%, still more preferably at least 90 wt.-% and further preferably at least 95 wt.-%.

A relatively large proportion of the ZrO_2 contained in the catalyst support according to the invention is present in the tetragonal modification. Tetragonal zirconium dioxide has a relatively high specific surface area. However, the phase stable at room temperature is monoclinic zirconium dioxide which has a relatively low specific surface area. Surprisingly, by simply incorporating undoped zirconium hydroxide into a support matrix comprising a sheet silicate followed by calcining, the surface-rich tetragonal ZrO_2 phase was successfully produced in a high yield and stabilized. Thus, a relatively high zirconium dioxide specific surface area is provided in the catalyst support according to the invention using relatively little expensive zirconium. The

catalyst support known from the state of the art which is prepared by impregnating a catalyst support with a zirconium salt solution followed by calcining is X-ray amorphous as regards the zirconium. This normally means that the zirconium is present in the form of nanocrystalline particles and/or in amorphous form.

Accordingly, it is provided according to a further preferred embodiment of the catalyst support according to the invention that at least 50 wt.-% of the ZrO_2 contained in the catalyst support according to the invention is present in the tetragonal modification, preferably 50 wt.-% to 100 wt.-%, more preferably 70 wt.-% to 99 wt.-%, still more preferably 85 wt.-% to 98 wt.-%, further preferably 90 wt.-% to 97 wt.-%, further preferably 92 wt.-% to 96 wt.-% and still further preferably 93 wt.-% to 95 wt.-%. The above proportions again relate to the X-ray diffraction active ZrO_2 contained in the support. A proportion of 100 wt.-% of tetragonal ZrO_2, which is particularly preferred according to the invention, means that only signals from tetragonal ZrO_2 can be identified in a corresponding XRD spectrum and no signals from ZrO_2 of monoclinic or cubic modification.

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that in an XRD spectrum of the support the ratio of the intensity of the signal at 2 theta of 28.2° to the intensity of the signal at 2 theta of 30.2° is less than/equal to 1, preferably less than 0.5, preferably less than 0.3, still more preferably less than 0.05 and still further preferably equal to 0. It is furthermore preferred that the XRD spectrum of the support is free of signals from cubic ZrO_2. The peak of greatest intensity (hkl 111) of monoclinic ZrO_2 lies at 2 theta of 28.2°, the peak of greatest intensity (hkl 101) of tetragonal ZrO_2 lies at 2

theta of 30.2°. The XRD spectrum is a so-called XRD-difference spectrum. The XRD difference spectrum is generated by having an XRD spectrum of a catalyst support according to the invention and a reference catalyst support recorded under identical conditions and subtracting the XRD spectrum of the reference catalyst support from that of the catalyst support according to the invention. The reference catalyst support is prepared analogously to the catalyst support according to the invention, with the exception that Zr is not added to the reference catalyst support. The XRD spectra are preferably measured on an X-ray powder diffractometer from Bruker AXS, model D4 ENDEAVOR, in Bragg-Brentano geometry. The device parameters are preferably: Cu K_{alpha} 1.5406 Å, current voltage 40 kV, current strength 40 mA and the scan parameters are: continuous scan, 2 theta of 5° to 90°, step size = 0.03° 2 theta, time per step = 0.5 s, divergence slit = 12 mm variable, anti-scatter slit = 12 mm variable, sample rotation: 30 rpm.

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the ZrO_2 is present in particulate form.

If ZrO_2 is present in the catalyst support according to the invention in the tetragonal modification, the ZrO_2 is contained in the support in particulate form. Otherwise, the ZrO_2 can in principle also be contained in the support in the form of individual ZrO_2 units which are incorporated for example into the framework structure of the material. But it is preferred that the ZrO_2 is present in the catalyst support according to the invention in particulate form. A stable incorporation of the ZrO_2 in the material and thus a largely low solubility in acetic acid (Zr release) of the ZrO_2 contained in the catalyst support is thereby ensured.

If the ZrO_2 is contained in the catalyst support according to the invention in particulate form, it is provided according to a further preferred embodiment of the catalyst support according to the invention that the ZrO_2 has an average particle diameter d_{50} of at most 50 µm, preferably an average particle diameter d_{50} of at most 30 µm and further preferably an average particle diameter d_{50} of at most 20 µm. The average particle diameter d_{50} is determined by element distribution by means of electron microscopy (SEM/EDX). For this, the maximum dimensions of the 50 largest identifiable ZrO_2 particles in a 1 mm x 1 mm area selected at random, but representative of an EDX spectrum of the catalyst support, are measured and the d_{50} value calculated from them. The EDX measurement preferably takes place on a LEO 1530VP scanning electron microscope equipped with an energy-dispersive spectrometer from Bruker AXS. For the measurement, the catalyst support is cut through, and glued to a graphite sample holder. A nitrogen-free silicon drift chamber detector (XFlash® 4010) with an energy resolution of 129 eV for the manganese K_{alpha} line at 130 kcps is preferably used as detector.

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the ZrO_2 is contained statistically evenly distributed in the material.

It was found that the more evenly distributed the ZrO_2 contained in the matrix of the support, the greater the achievable mechanical stability of the catalyst support. It was also found that catalyst supports with even distribution of the ZrO_2, not only as spheres but also in the form of hollow cylinders or trilobes, have good mechanical stability. According to a further preferred embodiment of the catalyst

support according to the invention, it is therefore provided that the ZrO_2 is contained evenly distributed, preferably homogeneously or statistically evenly distributed, in the material.

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the ZrO_2 is contained in the catalyst support in a proportion of 1 wt.-% to 30 wt.-%, relative to the weight of the catalyst support.

If ZrO_2 is contained in the catalyst support in a proportion of less than 1 wt.-%, the alkenyl acetate activity of a corresponding catalyst according to the invention is increased only slightly, while above a proportion of 30 wt.-% the increase in the activity of the catalyst can be accompanied by a noticeable loss of alkenyl acetate selectivity. Accordingly, it is provided according to a further preferred embodiment of the catalyst support according to the invention that the ZrO_2 is contained in the catalyst support in a proportion of 1 wt.-% to 30 wt.-%, relative to the weight of the catalyst support, preferably in a proportion of 5 wt.-% to 20 wt.-% and further preferably in a proportion of 8 wt.-% to 15 wt.-%.

According to a further preferred embodiment of the catalyst support according to the invention it is provided that the ZrO_2 particles are contained evenly distributed in the support and the support is free or essentially free of a percolation network of ZrO_2 particles.

According to a further preferred embodiment of the catalyst support according to the invention it is provided that the ZrO_2 particles are evenly distributed over the cross-section of the

support and that the support is free or essentially free of a percolation network of ZrO_2 particles.

In the catalyst support according to the invention the ZrO_2 content is preferably chosen according to the particle size of the resulting ZrO_2 particles in the support such that the percolation threshold in the support matrix is not reached. As is clear for example from the following EDX photographs, the ZrO_2 particles are essentially present as discrete units, not linked with each other and statistically evenly distributed in the support matrix. By percolation threshold within the meaning of percolation theory (see Stauffer D. and Aharony A. : ***Introduction to Percolation Theory***, Taylor and Francis, London, 1994) is meant any threshold relating to the concentration of ZrO_2 in the catalyst support, wherein for the first time a three-dimensional ZrO_2 network passes completely through the support. It is assumed that when the percolation threshold is exceeded during impregnation of a corresponding support with metal salt solutions, the diffusion runs into the support matrix along the ZrO_2 units, which leads to a higher or more uneven introduction of metal salt solution into the support core and thus hinders the formation of shell catalysts.

A natural sheet silicate is contained in the catalyst support according to the invention. By "natural sheet silicate", for which the term "phyllosilicate" is also used in the literature, is meant within the framework of the present invention untreated or treated silicate mineral from natural sources, in which SiO_4 tetrahedra, which form the structural base unit of all silicates, are cross-linked with each other in layers of the general formula $[Si_2O_5]^{2-}$. These tetrahedron layers alternate with so-called octahedron layers in which a cation, principally Al and Mg, is octahedrally surrounded by

OH or O. A distinction is drawn for example between two-layer phyllosilicates and three-layer phyllosilicates. Sheet silicates preferred within the framework of the present invention are clay minerals, in particular kaolinite, beidellite, hectorite, saponite, nontronite, mica, vermiculite and smectites, wherein smectites and in particular montmorillonite are particularly preferred. Definitions of the term "sheet silicates" are to be found for example in "Lehrbuch der anorganischen Chemie", Hollemann Wiberg, de Gruyter, 102nd edition, 2007 (ISBN 978-3-11-017770-1) or in "Römpp Lexikon Chemie", 10th edition, Georg Thieme Verlag under the headword "Phyllosilikat".

Typical treatments to which a natural sheet silicate is subjected before use as support material include in particular a treatment with acids, in particular mineral acids such as for example hydrochloric acid, and/or calcining.

A natural sheet silicate particularly preferred within the framework of the present invention is montmorillonite, which is preferably used in the form of a bentonite. Bentonites are mixtures of different clay minerals which contain as predominant component montmorillonite (approximately 50 wt.-% to 90 wt.-%). Further accompanying minerals can be i.a. quartz, mica and feldspar.

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the natural sheet silicate is an acid-activated sheet silicate.

Acid-activated sheet silicates are known in the state of the art (cf. Römpp Lexikon Chemie, 10th edition, Georg Thieme Verlag, headword "Bentonite"). In order to increase the adsorption force of the catalyst support according to the

invention, the natural sheet silicate is preferably present in the support in the form of an acid-activated sheet silicate. It is further preferred that the acid-activated sheet silicate is acid-activated montmorillonite which according to the invention is further preferably contained in the support according to the invention in the form of an acid-activated bentonite.

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the catalyst support has an acidity of 1 μval/g to 150 μval/g.

The degree of acidity of the catalyst support according to the invention can, at least indirectly, advantageously influence the performance of a corresponding catalyst with regard to the gas-phase synthesis of alkenyl acetates from acetic acid and ethene. According to a further preferred embodiment of the catalyst support according to the invention, it is therefore provided that the catalyst support has an acidity of 1 μval/g to 150 μval/g, preferably an acidity of 5 μval/g to 130 μval/g, preferably an acidity of 10 μval/g to 100 μval/g and particularly preferably an acidity of 20 μval/g to 60 μval/g. The acidity of the support can for example be increased by impregnating the support with acid.

The acidity of a catalyst support is determined as follows: 100 ml water (with a pH blank value) is added to 1 g of the finely ground catalyst support and extraction carried out for 15 minutes accompanied by stirring. Titration to at least pH 7.0 with 0.01 n NaOH solution follows, wherein the titration is carried out in stages; 1 ml of the NaOH solution is firstly added dropwise to the extract (1 drop/second), followed by a 2-minute wait, the pH is read, a further 1 ml NaOH added dropwise, etc. The blank value of the water used is determined

and the acidity calculation corrected accordingly. The titration curve (ml 0.01 NaOH against pH) is then plotted and the intersection point of the titration curve at pH 7 determined. The mole equivalents which result from the NaOH consumption for the intersection point at pH 7 are calculated in 10^{-6} equiv/g support:

Total acid: $$\frac{\text{10 * ml 0.01 n NaOH}}{\text{1 Support}} = \mu\text{val/g}$$

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the catalyst support has an average pore diameter of 8 nm to 30 nm.

To keep the pore diffusion limitation of the catalyst support according to the invention largely small, it is provided according to a further preferred embodiment of the catalyst according to the invention that the catalyst support has an average pore diameter of 7 nm to 30 nm, preferably of 9.5 nm to 20 nm and particularly preferably of 10.5 nm to 15 nm and most preferably of 11.5 to 13.5 nm. The average pore diameter is determined according to DIN 66134 (determination of the pore-size distribution and specific surface area of mesoporous solids by nitrogen sorption (process according to Barrett, Joyner and Halenda (BJH)).

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the catalyst support has a specific surface area of less than/equal to 180 m^2/g.

It has been established that, the smaller the specific surface area of a catalyst support according to the invention, the higher the alkenyl acetate selectivity of an alkenyl acetate

catalyst prepared using the catalyst support according to the invention with a virtually constant activity of the catalyst. According to a particularly preferred embodiment of the catalyst support according to the invention, it is therefore provided that the catalyst support has a specific surface area of less than/equal to 180 m^2/g, preferably less than/equal to 160 m^2/g, preferably less than/equal to 140 m^2/g, further preferably less than/equal to 137 m^2/g, more preferably less than/equal to 135 m^2/g, still more preferably less than/equal to 133 m^2/g and particularly preferably less than/equal to 130 m^2/g. The specific surface area of the support according to the invention is determined according to DIN 66131 (determination of the specific surface area of solids by gas adsorption according to Brunauer, Emmett and Teller (BET)) by means of nitrogen.

According to the invention, it is furthermore preferred that the catalyst support has a specific surface area of 60 m^2/g to 180 m^2/g, preferably of 65 m^2/g to 160 m^2/g, preferably of 70 m^2/g to 150 m^2/g, further preferably of 75 m^2/g to 140 m^2/g, more preferably of 75 m^2/g to 130 m^2/g and most preferably of 80 m^2/g to 120 m^2/g.

The size of the specific surface area, of the average pore diameter, of the integral pore volume, etc. of the catalyst support depends in particular on the quality of the natural sheet silicate used, the acid-treatment method, i.e. for example the nature and the quantity, relative to the sheet silicate, and the concentration of the mineral acid used, the acid-treatment duration and temperature, on the moulding pressure and on the calcining duration and temperature and also the calcining atmosphere.

The catalyst support according to the invention has a relatively high stability. According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the catalyst support has a hardness greater than/equal to 30 N, preferably a hardness of 50 N to 75 N and particularly preferably a hardness of 55 N to 70 N. The hardness (indentation hardness) is measured on spherical samples (diameter: 5 mm) by means of the 8M tablet-hardness testing machine from Dr. Schleuniger Pharmatron AG (Switzerland). Before measurement the samples are dried over a period of 2 h at a temperature of 130°C. The hardness is calculated as the average of 99 measurements. For the measurements the choosable parameters, named below, of the 8M tablet-hardness testing machine are set as follows:

Hardness (dimension):	N
Distance from the sample:	5.00 mm
Time delay:	0.80 s
Feed type:	6 D
Speed:	0.60 mm/s

According to the invention, it is preferred that the proportion of natural sheet silicate in the catalyst support according to the invention is more than/equal to 50 wt.-%, preferably 55 wt.-% to 99 wt.-%, preferably 60 wt.-% to 97 wt.-%, further preferably 65 wt.-% to 95 wt.-% and still further preferably 70 wt.-% to 90 wt.-%, relative to the weight of the catalyst support.

According to a further preferred embodiment of the catalyst support according to the invention it is provided that the catalyst support has an integral pore volume of 0.25 ml/g to 0.7 ml/g.

Compared with a catalyst support of the state of the art, which has been surface-doped with ZrO_2 by means of a zirconium salt solution, the catalyst support according to the invention has a relatively large pore volume, as, when ZrO_2 is introduced during the preparation of the catalyst support according to the invention, the pores of the support are not blocked. It was found that the alkenyl acetate selectivity of an alkenyl acetate catalyst prepared by means of the catalyst support according to the invention depends on the integral pore volume of the catalyst support. It is therefore preferred that the catalyst support has an integral pore volume of 0.25 ml/g to 0.7 ml/g, preferably 0.3 ml/g to 0.65 ml/g and preferably 0.30 ml/g to 0.50 ml/g. The integral pore volume is determined according to DIN 66134 (determination of the pore-size distribution and specific surface area of mesoporous solids by nitrogen sorption (process according to Barrett, Joyner and Halenda (BJH)).

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that at least 80%, preferably at least 90%, preferably at least 98% and most preferably at least 99%, of the integral pore volume of the catalyst support is formed from mesopores and macropores. A reduced activity, effected by diffusion limitation, of an alkenyl acetate catalyst prepared by means of the catalyst support according to the invention, in particular a Pd/Au shell catalyst with relatively large shell thickness is thereby counteracted. By "micropores", "mesopores" and "macropores" are meant pores which have a diameter of less than 2 nm, a diameter of 2 nm to 50 nm and a diameter of more than 50 nm respectively. The volume proportion of the mesopores and macropores in the integral pore volume is ascertained using the pore-volume distribution of the catalyst support according to the invention, which is

determined according to DIN 66134 (determination of the pore-size distribution and specific surface area of mesoporous solids by nitrogen sorption (process according to Barrett, Joyner and Halenda (BJH)).

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the proportion of the integral pore volume accounted for by pores of the support with a diameter of 6 nm to 50 nm is more than 66%, preferably 66% to 80% and particularly preferably 68% to 75%. The percentages are calculated from the pore-size distribution which is to be determined according to DIN 66134 (determination of the pore-size distribution and specific surface area of mesoporous solids by nitrogen sorption (process according to Barrett, Joyner and Halenda (BJH)).

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the catalyst support has a bulk density of more than/equal to 0.4 g/ml, preferably more than/equal to 0.45 g/ml, preferably more than/equal to 0.6 g/ml and particularly preferably a bulk density of 0.6 g/ml to 0.75 g/ml.

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the natural sheet silicate contained in the catalyst support has an SiO_2 content of at least 65 wt.-%, preferably at least 80 wt.-% and particularly preferably 85 wt.-% to 97 wt.-%. A high chemical resistance of the catalyst support according to the invention in the alkenyl acetate synthesis is thereby ensured.

In the gas-phase synthesis of an alkenyl acetate from acetic acid and ethene, a relatively low Al_2O_3 content in the natural

sheet silicate is scarcely disadvantageous, whereas with high Al_2O_3 contents a marked reduction in the indentation hardness of the catalyst support must be expected. According to a preferred embodiment of the catalyst support according to the invention, the natural sheet silicate therefore contains less than 5 wt.-% Al_2O_3, preferably 0.1 wt.-% to 3 wt.-% and preferably 0.3 wt.-% to 2.50 wt.-%, relative to the weight of the natural sheet silicate contained in the support according to the invention.

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the catalyst support is formed as a shaped body.

In particular with regard to the preparation of shell catalysts it is favourable that the catalyst support according to the invention is formed as a shaped body. In principle the catalyst support can have any form known to a person skilled in the art to be suitable for the purpose according to the invention. For example the catalyst support according to the invention can be formed as a sphere, cylinder, perforated cylinder, trilobe, ring, star, torus or strand, preferably as a sphere, perforated cylinder, or trilobe.

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the catalyst support has a maximum size of 1 mm to 25 mm, preferably a maximum size of 3 mm to 15 mm.

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the catalyst support is formed as a sphere.

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that the sphere has a diameter of 2 mm to 10 mm, preferably a diameter of 4 mm to 8 mm.

According to a further embodiment of the catalyst support according to the invention, it is provided that the catalyst support is doped with at least one oxide of a metal selected from the group consisting of Hf, Ti, Nb, Ta, W, Mg, Re, Y and Fe, preferably with HfO_2. The activity of an alkenyl acetate catalyst prepared using the catalyst support according to the invention can be increased by the doping.

It can be provided that the catalyst support is doped with Y_2O_3 and/or HfO_2. A high level of stabilization of the tetragonal modification of the ZrO_2 accompanied by a high resistance of the ZrO_2 to acetic acid is ensured by the Y_2O_3 doping. The HfO_2 doping effects an increase in the activity of a corresponding alkenyl acetate catalyst. The ZrO_2 itself can be doped with Y_2O_3, HfO_2 or HfO_2 and Y_2O_3. The proportion of Y_2O_3 in the doped ZrO_2 can amount to 1 wt.-% to 8 wt.-%, preferably 3 wt.-% to 5 wt.-%, and the proportion of HfO_2 in the ZrO_2 to 0.1 wt.-% to 5 wt.-%, preferably 1 wt.-% to 2 wt.-%. According to the invention it is however particularly preferred that the ZrO_2 contained in the catalyst support is free of doping oxide stabilizing the tetragonal phase, in particular free of Y_2O_3. Even without doping with a metal oxide stabilizing the tetragonal phase, the tetragonal ZrO_2 in the support according to the invention is stable.

It is provided according to a further preferred embodiment of the catalyst support according to the invention that the proportion of doping oxide in the catalyst support is between 1 wt.-% and 20 wt.-%, preferably 2 wt.-% to 10 wt.-%, and

preferably 3 wt.-% to 8 wt.-%, relative to the weight of the catalyst support. The doping can take place for example by surface doping, such as is known from the state of the art, or the metal oxide(s) can be incorporated into the matrix of the catalyst support.

According to a further preferred embodiment, it can be provided that the water absorbency of the catalyst support is 40% to 75%, preferably 50% to 70%, calculated as the weight increase due to water absorption. The absorbency is determined by steeping 10 g of the support sample in deionized water for 30 min until gas bubbles no longer escape from the support sample. The excess water is then decanted and the steeped sample blotted with a cotton towel to remove adhering moisture from the sample. The water-laden support is then weighed and the absorbency calculated as follows:

(amount weighed out (g) – amount weighed in (g)) × 10 = water absorbency (%)

The present invention also relates to a process, in particular for the preparation of a catalyst support according to the invention, comprising

- the preparation of a mixture, comprising a powdery natural sheet silicate and powdery zirconium hydroxide;

- the calcining of the mixture at a temperature above 620°C.

It was found that a catalyst support prepared by means of the process according to the invention has a relatively low solubility in acetic acid of the ZrO_2 contained in the catalyst (Zr release), with the result that relatively little ZrO_2 needs

to be contained in the catalyst support in order to maintain the increased activity of a corresponding alkenyl acetate catalyst over a relatively long period. In boiling acetic acid the catalyst supports prepared by means of the process according to the invention have a solubility in acetic acid of the ZrO_2 contained in the catalyst support of less than 0.06 wt.-% to 0.0001 wt.-%, relative to the weight of the ZrO_2 contained in the catalyst support. The solubility in acetic acid of the ZrO_2 contained in the catalyst support is determined as already explained above.

It was also found that 50% to 100% of the X-ray diffraction active ZrO_2 contained in a catalyst support prepared by means of the process according to the invention is present in the tetragonal modification.

According to a further preferred embodiment of the process according to the invention it is provided that the natural sheet silicate is an acid-activated natural sheet silicate.

In the process according to the invention a mixture is prepared, which contains a powdery natural sheet silicate and powdery zirconium hydroxide. The natural sheet silicate may be an acid-activated natural sheet silicate. Acid-activated natural sheet silicates are known in the state of the art (cf. Römpp Lexikon Chemie, 10^{th} edition, Georg Thieme Verlag, headword "Bentonite"). They are prepared by treating a natural sheet silicate with a mineral acid, preferably with hydrochloric acid.

According to a further preferred embodiment of the process according to the invention it is provided that the powdery zirconium hydroxide has a d_{10} value between 0.1 µm and 3.0 µm,

a d_{50} value between 0.5 µm and 10 µm and a d_{90} value between 1.0 µm and 20 µm.

It was found that the mechanical stability of a catalyst support prepared by means of the process according to the invention depends on the particle-size distribution of the zirconium hydroxide used. If a powdery zirconium hydroxide is used in the process according to the invention, with a d_{10} value between 0.1 µm and 3.0 µm, with a d_{50} value between 0.5 µm and 10 µm and with a d_{90} value between 1.0 µm and 20 µm, catalyst supports are obtained, which – preferably formed as 5 mm spheres - are characterized by an extremely high mechanical stability of up to more than 55 N. Overall, however, as the ZrO_2 content in the catalyst support increases, lower mechanical stabilities can be determined. In the case of the use of shaped bodies of a size greater than 5 mm or of cylindrical shaped bodies, mechanical stabilities of more than 90 N, preferably more than 120 N can also be obtained.

According to a further preferred embodiment of the process according to the invention it is provided that the average particle diameter d_{50} of the powdery sheet silicate used is greater than that of the zirconium hydroxide used.

It was found that the mechanical stability of a catalyst support prepared by means of the process according to the invention is greater if the average particle diameter d_{50} of the natural sheet silicate used in the process according to the invention is greater than the average particle diameter d_{50} of the zirconium hydroxide used, at least the majority of which is converted into the tetragonal ZrO_2 during the process according to the invention. According to a further preferred embodiment of the process according to the invention it is therefore provided that the average particle diameter of the

sheet silicate is greater than that of the zirconium hydroxide.

The average particle diameter d_{50} of the raw materials (and also the d_{10} and d_{90} value) is determined by means of lasers on a Master Sizer (Malvern Instruments, GB) according to the standard method (other measuring apparatus includes e.g. Horiba LA 500 (Horiba Ltd., JP) or Helos (Sympatec GmbH, DE), which use the same measurement principle). For this, the $Zr(OH)_4$ or sheet silicate samples are introduced into a vessel with water, and this vessel is then placed in the measuring apparatus. The measuring procedure is automatic and also includes the mathematical determination of the d_{50} value. The d_{50} value is by definition determined from the (relative) cumulative curve of the particle-size distribution, wherein the intersection point of the 50 wt.-% y-coordinate with the cumulative curve on the x-axis provides the desired d_{50} value.

According to a further preferred embodiment of the process according to the invention it is provided that the calcining is carried out at a temperature of 620°C to 800°C.

It was found that a catalyst support prepared by means of the process according to the invention is characterized by a particularly low solubility of ZrO_2 in acetic acid and thus by a low loss of Zr in the alkenyl acetate preparation process, if the mixture comprising the natural sheet silicate and zirconium hydroxide is calcined at a temperature of 620°C to 800°C, preferably at a temperature of 630°C to 750°C, preferably at a temperature of 650°C to 700°C. The zirconium hydroxide is converted into ZrO_2 during the calcining of the mixture.

It was also found that the yield of zirconium, expressed as ZrO_2 yield, in the catalyst support is particularly high due to calcining in the temperature range described above. The ZrO_2 yield relates to the ZrO_2 content of the catalyst support after the first calcining and after treatment with mineral acid. The ZrO_2 yield is determined as follows:

ZrO_2 yield = Zr content in the catalyst support (converted into ZrO_2) after the mineral acid treatment * quantity of catalyst support obtained / quantity of Zr used (converted to ZrO_2). The ZrO_2 yield of a catalyst support prepared by means of the process according to the invention amounts to at least 85%, preferably at least 95% and most preferably at least 97%.

According to a further preferred embodiment of the process according to the invention, it is provided that the calcining is carried out over a period of 3 h to 24 h.

In order to ensure a largely complete conversion of the zirconium hydroxide used in the process according to the invention into ZrO_2 and a largely complete formation of the tetragonal modification of the ZrO_2, the mixture to be used in the process according to the invention is calcined over a period of at least 3 h, preferably over a period of 3 h to 24 h and particularly preferably over a period of 5 h to 10 h.

According to a further preferred embodiment of the process according to the invention it is provided that the mixture is moulded into a shaped body before the calcining. The mixture can be moulded into shaped bodies by means of any process and any device known to a person skilled in the art to be suitable for the purpose according to the invention. The moulding of shaped bodies can thus for example be carried out by means of a tablet press.

According to a further preferred embodiment of the process according to the invention, it is provided that the mixture is treated with a mineral acid after the calcining.

In order to clean the solid mixture obtained after the calcining and in particular to remove the majority of residual ZrO_2 which is soluble in acetic acid, it is provided according to a further preferred embodiment of the process according to the invention that the mixture is treated with a mineral acid after the calcining. There can be used as mineral acids any mineral acids which are known to a person skilled in the art to be suitable for the purpose according to the invention. Examples of preferred mineral acids are hydrochloric acid, nitric acid, sulphuric acid and phosphoric acid, preferably in each case with a pH value of less than pH=2, more preferably with a pH value of less than pH=1.

According to a further preferred embodiment of the process according to the invention, it is provided that the mineral acid is hydrochloric acid.

It was found that the calcined mixture resulting from the process according to the invention can be particularly effectively purified with hydrochloric acid, for example with 10-30% hydrochloric acid. According to a further preferred embodiment of the process according to the invention, it is accordingly provided that the mineral acid is hydrochloric acid.

According to a further preferred embodiment of the process according to the invention, it is provided that the calcined mixture is washed after the treatment with mineral acid.

In order, after the treatment with mineral acid, to remove acid residues and components, dissolved out of the natural sheet silicate by the mineral acid, from the calcined mixture, the calcined mixture is washed after the treatment with acid, preferably with water.

According to a further preferred embodiment of the process according to the invention, it is provided that the calcined mixture is again calcined after the washing.

According to a further preferred embodiment of the process according to the invention it is provided that the calcined mixture is again calcined after the washing, preferably at a temperature of 400°C to 800°C, preferably at a temperature of 500°C to 600°C. The second calcining step has the effect of further reducing the Zr release of the material.

The present invention also relates to a catalyst support which can be obtained according to the process according to the invention.

According to a preferred embodiment of the catalyst support which can be obtained by means of the process according to the invention, it is provided that the catalyst support comprises a natural sheet silicate and ZrO_2 in the tetragonal modification, wherein it is further preferred that at least 50 wt.-% of the ZrO_2 contained in the catalyst support is present in the tetragonal modification, preferably 90 wt.-% and particularly preferably 95 wt.-% to 100 wt.-%.

The present invention furthermore relates to a catalyst support with an XRD spectrum according to Figure 2.

The present invention furthermore relates to the use of the first catalyst support according to the invention and of the second catalyst support according to the invention and of the catalyst support which can be obtained by means of the process according to the invention and of the catalyst support according to the invention characterized by the XRD spectrum of Figure 2 in the preparation of a catalyst for the synthesis of alkenyl acetates.

According to a preferred embodiment of the use according to the invention, it is provided that the catalyst is a shell catalyst in the shell of which Pd and Au of the oxidation number 0 are contained.

The examples below serve, in conjunction with the drawing, to describe the invention. There are shown in:

Fig. 1: Section of an EDX photograph of a first catalyst support according to the invention according to example 1;

Fig. 2: XRD spectrum of the first catalyst support according to the invention;

Fig. 3: Section of an EDX photograph of a second catalyst support according to the invention according to example 1a;

Fig. 4: XRD spectrum of a catalyst support of the state of the art according to example 4;

Fig. 5: Section of an EDX photograph of the catalyst support according to example 4.

Example 1:

500.0 g of an acid-treated dried powdery bentonite (acid-activated bentonite) with the main constituent montmorillonite as sheet silicate was mixed with a quantity of $Zr(OH)_4$ customary in the trade corresponding to 61.875 g of ZrO_2, with a d_{10} value of approx. 1 µm, a d_{50} value of approx. 5 µm and with a d_{90} value of 7 µm, and also with 10 g of a customary organic binder/pore-forming agent.

Water was added to the resultant mixture and it was processed by means of a mixer into a dough from which spherical shaped bodies (d = 5 mm) were prepared under pressure by means of a tablet press. For hardening, the spheres were dried and calcined at a temperature of 650°C over a period of 5 h. After the calcining, the shaped bodies were treated with 20% hydrochloric acid over a period of 30 h, washed with plenty of water and calcined at a temperature of 600°C over a period of 5 h. The thus-obtained shaped bodies have the characteristics listed in Table 1:

Table 1:

Geometric form	Sphere
Diameter	5 mm
Moisture content	0.5 wt.-%
Compressive strength	60 N
Bulk density	607 g/l
Water absorbency	58%
Specific surface area (BET)	133 m^2/g
SiO_2 content	81.6 wt.-%
ZrO_2 content	12.8 wt.-%
ZrO_2 yield	98%
Proportion of tetragonal ZrO_2 (determined according to XRD diffractogram)	> 90 wt.-%
Al_2O_3 content	2.5 wt.-%
Loss on ignition 1000°C	1.5 wt.-%
Acidity	62 µval
Integral pore volume	0.377 ml/g
Zr release	0.001 wt.-%
Average pore diameter (according to BJH) (4V/A)	10.5 nm
Proportion of the integral pore volume accounted for by micropores	< 1%
Proportion of the integral pore volume accounted for by pores with a diameter of 2.0 nm to 6 nm	14.3%
Proportion of the integral pore volume accounted for by pores with a diameter of 6.0 nm to 50 nm	70.2%
Proportion of the integral pore volume accounted for by pores with a diameter of 2.0 nm to 50 nm	84.5%
Average particle size d_{50} of the ZrO_2 (determined from EDX mapping)	20 µm

A catalyst support according to example 1 was halved and the cut surface of one half measured by means of energy-dispersive X-ray spectroscopy (EDX). Figure 1 shows a section of the EDX photograph. The homogeneous statistical distribution of the ZrO_2 particles (dark spots) in the support matrix is clearly visible.

A catalyst support according to example 1 was ground to a powder and measured by X-ray diffractometry. The resulting XRD spectrum is shown in Figure 2. Only signals from tetragonal ZrO_2 can be identified in the XRD spectrum. No monoclinic or cubic ZrO_2 can be identified in the spectrum.

Example 1a:

Catalyst supports were prepared analogously to example 1, differing only in that a quantity of $Zr(OH)_4$ customary in the trade corresponding to 132 g of ZrO_2 was used. The thus-obtained shaped bodies have the characteristics listed in Table 1a:

Table 1a:

Geometric form	Sphere
Diameter	5 mm
Moisture content	0.4 wt.-%
Compressive strength	33 N
Bulk density	580 g/l
Water absorbency	67.1%
Specific surface area (BET)	132 m^2/g
SiO_2 content	69.5 wt.-%
ZrO_2 content	24.5 wt.-%
ZrO_2 yield	99%
Proportion of tetragonal ZrO_2 (determined according to XRD diffractogram)	> 90 wt.-%
Al_2O_3 content	1.8 wt.-%
Loss on ignition 1000°C	1.6 wt.-%
Acidity	23 µval
Integral pore volume	0.4 ml/g
Zr release	0.001 wt.-%
Average pore diameter (according to BJH) (4V/A)	11.0 nm
Proportion of the integral pore volume accounted for by micropores	< 1%
Proportion of the integral pore volume accounted for by pores with a diameter of 2.0 nm to 6 nm	13.6%
Proportion of the integral pore volume accounted for by pores with a diameter of 6.0 nm to 50 nm	71.7%
Proportion of the integral pore volume accounted for by pores with a diameter of 2.0 nm to 50 nm	85.3%
Average particle size d_{50} of the ZrO_2 (determined from EDX mapping)	20 µm

A catalyst support according to example 1a was halved and the cut surface of one half measured by means of EDX. Figure 3 shows a section of the EDX photograph. The homogeneous statistical distribution of the ZrO_2 particles (light spots) in the support matrix is clearly visible.

Example 1b:

Catalyst supports were prepared analogously to example 1, differing only in that the catalyst supports were treated with hydrochloric acid for a period of only 8 h. The thus-obtained shaped bodies have the selected characteristics listed in Table 1b:

Table 1b:

ZrO_2 content	12.6 wt.-%
Proportion of tetragonal ZrO_2 (determined according to XRD diffractogram)	> 90 wt.-%
Zr release	0.002 wt.-%
Average pore diameter (according to BJH) (4V/A)	7.7 nm
ZrO_2 yield	98.5%

Example 2:

Catalyst supports were prepared analogously to example 1, differing in that the first calcining was carried out after the shaping at only 550°C. The thus-obtained shaped bodies have the selected characteristics listed in Table 2:

Table 2:

ZrO_2 content	9.6 wt.-%
Zr release	0.001 wt.-%
Average pore diameter (according to BJH) (4V/A)	11.0 nm
ZrO_2 yield	76%

The thus-obtained support has a ZrO_2 yield of only 76% and a ZrO_2 content of 9.6 wt.-%.

Example 3 (comparison example):

A catalyst support commercially available from Süd-Chemie AG, Munich, Germany with the trade name "KA-160" for example has the characteristics listed in Table 3:

Table 3:

Geometric form	Sphere
Diameter	5 mm
Water absorbency	66.4%
Specific surface area (BET)	161 m^2/g
SiO_2 content	91.8 wt.-%
Al_2O_3 content	3.6 wt.-%
Average pore diameter (according to BJH) (4V/A)	10.3 nm
Integral pore volume	0.436 ml/g
Proportion of the integral pore volume accounted for by pores with a diameter of 2.0 nm to 6 nm	11.0%
Proportion of the integral pore volume accounted for by pores with a diameter of 6.0 nm to 50 nm	71.6%
Proportion of the integral pore volume accounted for by pores with a diameter of 2.0 nm to 50 nm	82.7%

Example 4 (comparison example):

(cf. US 5,808,136) 74.6 g of an aqueous solution of zirconyl acetate ($ZrO(OAc)_2$), which had a Zr content of 15.5 wt.-% was diluted with approx. 8.5 ml of water. 100 g of the catalyst support KA-160 from Süd-Chemie AG according to example 3 was impregnated with the above solution. The impregnated support was dried and calcined at 500°C. The resulting catalyst support had a zirconium content of approx. 10 wt.-% (calculated as corresponding to 13.53 wt.-% ZrO_2). Further characteristics of the support are listed in Table 4:

Table 4:

Geometric form	Sphere
Diameter	5 mm
Water absorbency	49.1%
Specific surface area (BET)	134 m^2/g
Zr content*	10.0 wt.-%
SiO_2 content	80.9 wt.-%
Zr release*	0.129 wt.-%
Al_2O_3 content	3.0 wt.-%
Average pore diameter (according to BJH) (4V/A)	9.1 nm
Integral pore volume	0.332 ml/g
Proportion of the integral pore volume accounted for by pores with a diameter of 2.0 nm to 6 nm	20.0%
Proportion of the integral pore volume accounted for by pores with a diameter of 6.0 nm to 50 nm	65.1%
Proportion of the integral pore volume accounted for by pores with a diameter of 2.0 nm to 50 nm	85.2%

*For calculation purposes, the ZrO_2 content of 13.53 wt.-% ascertained by calculation from the Zr content is used

Figure 4 shows the XRD spectrum of a catalyst support prepared according to example 4. It is clear from the spectrum that the Zr in the support is not present in an X-ray diffraction active oxide form.

A catalyst support according to example 4 was halved and the cut surface of one half measured by means of EDX. Figure 5 shows a section of the EDX photograph. No discrete zirconium-containing particles are visible.

Example 5 (comparison example):

Catalyst supports were prepared analogously to example 1, differing only in that 57.8 g of a 20% zirconyl nitrate solution diluted with 19.7 ml of water was used.
Characteristics of the thus-obtained support are listed in Table 5:

Table 5:

Zr content*	2.6 wt.-%
Zr release*	0.06 wt.-%

* For calculation purposes, the ZrO_2 content of 3.51 wt.-% ascertained by calculation from the Zr content is used.

Note: On drying, enriched zirconyl nitrate separates from the surface resulting in a high loss of zirconium.

Comparative overview:

In Table 6 the average pore diameter, the integral pore volume and proportions of particular pore sizes in the integral pore volume of examples 3, 4, 1 and 1a are compared.

Table 6:

Example	3	4	1	1a
Average pore diameter (according to BJH) (4V/A)	10.3 nm	9.1 nm	10.5 nm	11.0 nm
Integral pore volume	0.436 ml/g	0.332 ml/g	0.377 ml/g	0.40 ml/g
Proportion of the integral pore volume accounted for by pores with a diameter of 2.0 nm to 6 nm	11.0%	20.0%	14.3%	13.6%
Proportion of the integral pore volume accounted for by pores with a diameter of 6.0 nm to 50 nm	71.6%	65.1%	70.2%	71.7%
Proportion of the integral pore volume accounted for by pores with a diameter of 2.0 nm to 50 nm	82.7%	85.2%	84.5%	85.3%

The subsequent impregnation of the commercial KA-160 support of example 3 with Zr according to example 4 leads to a significant reduction in the integral pore volume and to a narrowing of pores. The proportion of pores of 2 nm to 6 nm increases significantly, at the expense of the mesopores greater than 6 nm. However, compared with the catalyst support of example 3, the catalyst support prepared according to the

invention and according to the process according to the invention according to examples 1 and 1a, despite doping with 12.8 wt.-% or 24.5 wt.-% ZrO_2, has an overall higher or at least comparable proportion of mesopores in the case of an increased average pore diameter.

The Zr releases of examples 1, 1a, 1b, 2, 4 and 5 are compared in Table 7.

Table 7:

Example	1	1a	1b	2	4	5
Zr release [wt.-%]	0.001	0.001	0.002	0.001	0.129	0.060

The catalyst supports of examples 1, 1a and 1b and 2 have a clearly reduced Zr release compared with examples 4 and 5.

Claims

1. Open-pore catalyst support, consisting of a material which comprises a natural sheet silicate and ZrO_2 in the tetragonal modification.

2. Catalyst support according to claim 1, characterized in that the catalyst support in boiling acetic acid releases less than 0.06 wt.-% Zr calculated as ZrO_2, relative to the weight of the ZrO_2 contained in the catalyst support.

3. Open-pore catalyst support, consisting of a material which comprises a natural sheet silicate and ZrO_2, characterized in that the catalyst support in boiling acetic acid releases less than 0.06 wt.-% Zr calculated as ZrO_2, relative to the weight of the ZrO_2 contained in the catalyst support.

4. Catalyst support according to one of claims 1 to 3, characterized in that at least 50 wt.-% of the ZrO_2 contained in the catalyst support is present in the tetragonal modification.

5. Catalyst support according to one of claims 1 to 4, characterized in that the ZrO_2 is present in particulate form.

6. Catalyst support according to one of claims 1 to 5, characterized in that the ZrO_2 is contained evenly distributed in the material.

7. Catalyst support according to one of claims 1 to 6, characterized in that the ZrO_2 is contained in the catalyst support in a proportion of 1 wt.-% to 30 wt.-%.

8. Catalyst support according to one of claims 5 to 7, characterized in that the ZrO_2 particles are evenly distributed over the cross-section of the support and in that the support is essentially free of a percolation network of ZrO_2 particles.

9. Catalyst support according to one of claims 1 to 8, characterized in that the natural sheet silicate is an acid-activated sheet silicate.

10. Catalyst support according to one of claims 1 to 9, characterized in that the catalyst support has an acidity of 1 μval/g to 150 μval/g.

11. Catalyst support according to one of claims 1 to 10, characterized in that the catalyst support has an average pore diameter of 7 nm to 30 nm.

12. Catalyst support according to one of claims 1 to 11, characterized in that the catalyst support has a specific surface area of less than/equal to 180 m^2/g.

13. Catalyst support according to one of claims 1 to 12, characterized in that the catalyst support has a specific surface area of 180 m^2/g to 60 m^2/g.

14. Catalyst support according to one of claims 1 to 13, characterized in that the catalyst support has a hardness greater than/equal to 30 N.

15. Catalyst support according to one of claims 1 to 14, characterized in that the proportion of natural sheet silicate in the catalyst support is at least 50 wt.-%, relative to the weight of the catalyst support.

16. Catalyst support according to one of claims 1 to 15, characterized in that the catalyst support has an integral pore volume of 0.25 ml/g to 0.7 ml/g.

17. Catalyst support according to one of claims 1 to 16, characterized in that at least 80% of the integral pore volume of the catalyst support is formed from mesopores and macropores.

18. Catalyst support according to one of claims 1 to 17, characterized in that the catalyst support has a bulk density of more than 0.45 g/ml.

19. Catalyst support according to one of claims 1 to 18, characterized in that the natural sheet silicate contained in the catalyst support has an SiO_2 content of at least 65 wt.-%.

20. Catalyst support according to one of claims 1 to 19, characterized in that the natural sheet silicate contained in the support contains less than 5 wt.-% Al_2O_3.

21. Catalyst support according to one of claims 1 to 20, characterized in that the catalyst support is formed as a shaped body.

22. Catalyst support according to one of claims 1 to 21, characterized in that the catalyst support has a maximum size of 1 mm to 25 mm.

23. Catalyst support according to claim 21 or 22, characterized in that the catalyst support is a sphere.

24. Catalyst support according to claim 23, characterized in that the sphere has a diameter of 2 mm to 10 mm.

25. Catalyst support according to one of claims 1 to 24, characterized in that the catalyst support is doped with at least one oxide of a metal selected from the group consisting of Hf, Ti, Nb, Ta, W, Mg, Re, Y and Fe.

26. Catalyst support according to claim 25, characterized in that the proportion of doping oxide in the catalyst support is 1 wt.-% to 20 wt.-%.

27. Process, comprising

- the preparation of a mixture, comprising a powdery natural sheet silicate and powdery zirconium hydroxide;

- the calcining of the mixture at a temperature above 620°C.

28. Process according to claim 27, characterized in that the natural sheet silicate is an acid-activated natural sheet silicate.

29. Process according to claim 27 or 28, characterized in that the powdery zirconium hydroxide has a d_{10} value between 0.1 µm and 3.0 µm, a d_{50} value between 0.5 µm and 10 µm and a d_{90} value between 1.0 µm and 20 µm.

30. Process according to one of claims 27 to 29, characterized in that the average particle diameter of the sheet silicate is greater than that of the zirconium hydroxide.

31. Process according to one of claims 27 to 30, characterized in that the calcining is carried out at a temperature of 620°C to 800°C.

32. Process according to one of claims 27 to 31, characterized in that the calcining is carried out over a period of 3 to 24 h.

33. Process according to one of claims 27 to 32, characterized in that the mixture is moulded into a shaped body before the calcining.

34. Process according to one of claims 27 to 33, characterized in that the mixture is treated with a mineral acid after the calcining.

35. Process according to claim 34, characterized in that the mineral acid is hydrochloric acid.

36. Process according to claim 34 or 35, characterized in that the calcined mixture is washed after the treatment with mineral acid.

37. Process according to claim 36, characterized in that the calcined mixture is again calcined after the washing.

38. Catalyst support which can be obtained according to a process according to one of claims 27 to 37.

39. Use of a catalyst support according to one of claims 1 to 26 or according to claim 38 in the preparation of a catalyst for the synthesis of alkenyl acetates.

40. Use according to claim 39, characterized in that the catalyst is a shell catalyst in the shell of which Pd and Au of the oxidation number 0 are contained.