

5        **Zirconium oxide-doped catalyst support, process for its  
preparation and catalyst containing a zirconium oxide-doped  
catalyst support**

The present invention relates to a porous catalyst support  
10 consisting of a material comprising a natural sheet silicate.

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

VAM is prepared predominantly in the gas phase from acetic  
20 acid and ethylene by reaction with oxygen, wherein the  
catalysts used for this synthesis preferably contain Pd and Au  
as active metals and also an alkali metal component as  
promoter, preferably potassium in the form of the acetate. In  
the Pd/Au system of these catalysts, the active metals Pd and  
25 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  
30 second active metal component.

Currently, VAM is predominantly prepared by means of so-called  
shell catalysts in which the catalytic active metals of the  
catalyst do not fully penetrate the catalyst support formed as  
35 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 support  
lying further inside are almost free of noble metals. With the

- 5 help of shell catalysts, a more selective reaction control is possible in many cases than with catalysts in which the supports are impregnated with the active components into the core of the support ("impregnated through").
- 10 The shell catalysts known in the state of the art for the preparation of VAM 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).
- 15 Catalyst supports based on titanium oxide or zirconium oxide are currently scarcely used, however, as these catalyst supports do not display long-term stability compared with acetic acid and are relatively expensive.
- 20 The great majority of the catalysts currently used for the preparation of VAM are shell catalysts with a Pd/Au shell on a porous amorphous aluminosilicate support formed as a sphere based on natural sheet silicates in the form of natural acid-treated calcined bentonites which are thoroughly impregnated
- 25 with potassium acetate as promoter.

Such VAM shell catalysts are usually prepared by the so-called chemical route in which the catalyst support is loaded with or steeped in solutions of corresponding metal precursor

30 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 or steeped in a volume of solution corresponding to its pore volume. The Pd/Au shell of the catalyst is produced for example by first

35 steeping the catalyst support shaped body in a first step in an  $\text{Na}_2\text{PdCl}_4$  solution and then in a second step fixing the Pd component with NaOH solution 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  $\text{NaAuCl}_4$

5 solution and then the Au component is likewise fixed by means  
of NaOH. After the fixing of the noble-metal components in an  
outer shell of the catalyst support, the loaded catalyst  
support is then very largely washed free of chloride and Na  
ions, then dried, calcined and finally reduced with ethylene  
10 at 150°C. The thus-produced Pd/Au shell is usually  
approximately 100 to 500  $\mu\text{m}$  thick.

Usually, the catalyst support loaded with the noble metals is  
loaded with potassium acetate after the fixing or reducing  
15 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 with the  
promoter. A spherical support called "KA-160" from SÜD-Chemie  
AG based on natural acid-treated calcined bentonites as sheet  
20 silicate, which has a BET surface area of approximately 160  
 $\text{m}^2/\text{g}$ , is predominantly used as catalyst support.

The VAM selectivities, achieved by means of the VAM shell  
catalysts known in the state of the art based on Pd and Au as  
25 active metals and KA-160 supports as catalyst supports, are  
approximately 90 mol-% relative to the supplied ethylene,  
wherein the remaining 10 mol-% of the reaction products are  
essentially  $\text{CO}_2$  which is formed by total oxidation of the  
organic educts/products.

30 To increase the activity of these catalysts, the active-metal-  
free catalyst support shaped bodies based on natural silicates  
were firstly surface-doped with zirconium oxide before  
deposition of the noble metal. For this, for example, a  
35 finished bentonite-based shaped body was impregnated with a  
solution of a zirconium oxide precursor compound and the  
precursor compound converted into the corresponding oxide by  
calcining of the shaped body. Although, compared with the  
corresponding catalysts with a Pd/Au shell known in the state

5 of the art, such catalysts are characterized by an increased  
activity in respect of VAM production, the activity can be  
increased to only a limited extent, as the  $ZrO_2$  coats pores in  
which Pd and Au of oxidation stage 0 are also to be deposited.  
If the support is overloaded with  $ZrO_2$ , a decrease in the  
10 activity of the catalyst can be observed.

The object of the present invention is therefore to provide a  
catalyst support by means of which VAM catalysts can be  
prepared which are characterized by a relatively high VAM  
15 activity.

This object is achieved by a first porous catalyst support,  
consisting of a material comprising a natural sheet silicate,  
wherein  $ZrO_2$  is contained distributed in the material.

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Surprisingly it was found that, by incorporating  $ZrO_2$  into a  
material comprising a natural sheet silicate of which the  
matrix of the porous support is formed, catalyst supports can  
be obtained by means of which VAM catalysts can be prepared  
25 which are characterized by a relatively high VAM activity.

In addition, VAM catalysts prepared by means of the first  
catalyst support are characterized by a relatively high VAM  
selectivity and tend only slightly towards thermal aging over  
30 relatively long service lives.

The first catalyst support according to the invention is also  
characterized by a high chemical resistance in the VAM  
synthesis. While the  $ZrO_2$  incorporated into the sheet silicate  
35 matrix is largely resistant to acetic acid, and the support  
therefore displays a higher long-term stability and  
accordingly a corresponding catalyst has a high activity over  
long service lives, with supports of the state of the art the  
surface-impregnated  $ZrO_2$  is converted relatively quickly into

5    zirconyl acetate, which does not act as a promoter in the VAM synthesis, and washed out.

In addition, the catalyst support according to the invention is particularly cost-favourable. The preparation of the  
10   catalyst support according to the invention includes only one calcining step in which for example a mixture of a pulverant sheet silicate and a pulverant zirconium oxide precursor compound is calcined, and is thus in this respect more cost-favourable than a surface-doping of a previously calcined  
15   support with zirconium oxide precursor compounds followed by a second calcining or the application of zirconium oxide precursor compounds as suspensions to previously calcined supports (WO2005065821) and their subsequent calcining, wherein this process actually also requires an additional  
20   binder, usually zirconyl acetate, in order to obtain an adequate strength of the catalyst support.

A VAM catalyst prepared by means of the first catalyst support according to the invention is characterized by a particularly  
25   high VAM activity and selectivity if the  $\text{ZrO}_2$  is contained uniformly distributed, preferably homogeneously, in the material.

The  $\text{ZrO}_2$  can be contained in the material in the form of  
30   individual  $\text{ZrO}_2$  units which are integrated into the skeleton structure of the material. But it is preferred that the  $\text{ZrO}_2$  is present in particulate form. A firm incorporation of the  $\text{ZrO}_2$  in the material and thus a high thermal resistance to aging of a catalyst prepared by means of the first catalyst support  
35   according to the invention. The  $\text{ZrO}_2$  particles preferably have an average diameter of 1 nm to 100  $\mu\text{m}$ , preferably an average diameter of 0.5  $\mu\text{m}$  to 20  $\mu\text{m}$ .

5 Within the framework of the present invention, the terms  
"catalyst support shaped body", "catalyst support", "shaped  
body" and "support" are used synonymously.

The object according to the invention is further achieved by a  
10 second porous catalyst support, formed as a shaped body, with  
an outer shell, wherein the catalyst support, at least in the  
area of the outer shell, is formed from a matrix comprising a  
natural sheet silicate, in particular a matrix comprising an  
acid-treated calcined bentonite, in which zirconium oxide  
15 ( $\text{ZrO}_2$ ) particles are contained uniformly, preferably  
homogeneously, distributed.

The second catalyst support according to the invention  
displays the same advantages as the first catalyst support  
20 according to the invention.

It is preferred if the whole second catalyst support is formed  
from a matrix comprising a natural sheet silicate in which  
zirconium oxide ( $\text{ZrO}_2$ ) particles are contained uniformly  
25 distributed. The  $\text{ZrO}_2$  particles preferably have an average  
diameter of 1 nm to 100  $\mu\text{m}$ , preferably an average diameter of  
0.5  $\mu\text{m}$  to 20  $\mu\text{m}$ .

The present invention furthermore relates to a third porous  
30 catalyst support comprising a natural sheet silicate, wherein  
the catalyst support comprises at least 3 mass-% zirconium  
oxide, preferably in particulate form, wherein the  $\text{ZrO}_2$   
particles preferably have a diameter of 1 nm to 100  $\mu\text{m}$ ,  
preferably a diameter of 0.5  $\mu\text{m}$  to 20  $\mu\text{m}$ .

35 The preferred embodiments below relate both to the first and  
second and also to the third catalyst support according to the  
invention.

5 It is preferred that the zirconium oxide particles are  
contained in the catalyst support at a proportion of 1 to 25  
mass-%, preferably at a proportion of 3 to 20 mass-% and by  
preference at a proportion of 5 to 20 mass-% relative to the  
mass of the catalyst support. If the zirconium oxide is  
10 represented in the catalyst support at a proportion of less  
than 1 mass-%, the activity-increasing properties of the  
zirconium oxide have only a slight effect, while above a  
proportion of 25 mass-% the increase in activity of the  
catalyst can be accompanied by a clear decrease in VAM  
15 selectivity.

According to a preferred embodiment of the catalyst support  
according to the invention, its solubility in acetic acid is  
less than 8 wt.-%, preferably less than 4 wt.-% and  
20 particularly preferably less than 2 wt.-%. To determine acetic  
acid solubility, 5 g of the catalyst support are ground to  
powder and treated in 125 ml 96-% acetic acid (p.a.) for 1 h  
under reflux conditions. The catalyst support is separated off  
over a filter. The eluate is evaporated to dryness and the  
25 mass m (residue) of the solid residue determined and the  
acetic acid solubility calculated as follows: acetic acid  
solubility =  $(m(\text{residue})/5\text{g}) \cdot 100\%$ .

Low solubility values of the catalyst support according to the  
30 invention can be obtained by treating the catalyst support  
with acid after its preparation. Accordingly, according to a  
further preferred embodiment, the catalyst support is a  
support treated with an acid.

35 It is further preferred if the catalyst support displays an  
acidity of between 1 and 150  $\mu\text{val/g}$ , preferably between 5 and  
130  $\mu\text{val/g}$ , quite preferably between 10 and 100  $\mu\text{val/g}$  and  
particularly preferably between 10 and 60  $\mu\text{val/g}$ .

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The acidity of the catalyst support can advantageously influence the activity of the catalyst according to the invention during the gas phase synthesis of VAM from acetic acid and ethene. The acidity of the catalyst support is  
 10 determined as follows: 100 ml water (with a pH blank value) is added to 1 g of the finely ground catalyst support and extraction is 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  
 15 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.

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

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

In addition, it is preferred that the catalyst support has an  
 30 average pore diameter of 8 to 30 nm, preferably 9 to 20 nm and by preference 10 to 15 nm.

It was found that, the smaller the surface of the catalyst support according to the invention, the higher the VAM  
 35 selectivity of the catalyst according to the invention. By "surface" of the catalyst support is meant within the framework of the present invention the BET surface area of the

5 support, which is determined by means of adsorption of nitrogen according to DIN 66132.

Therefore it can be preferred that the catalyst support has a BET surface area less than/equal to  $145 \text{ m}^2/\text{g}$ , preferably less  
10 than/equal to  $142 \text{ m}^2/\text{g}$ , by preference less than/equal to  $140 \text{ m}^2/\text{g}$ , further preferably less than/equal to  $137 \text{ m}^2/\text{g}$ , more preferably less than/equal to  $135 \text{ m}^2/\text{g}$ , still more preferably less than/equal to  $133 \text{ m}^2/\text{g}$  and particularly preferably less than/equal to  $130 \text{ m}^2/\text{g}$ .

15 It is further preferred according to the invention that the catalyst support has a BET surface area of 60 to  $145 \text{ m}^2/\text{g}$ , preferably between 65 and  $140 \text{ m}^2/\text{g}$ , preferably between 70 and  $135 \text{ m}^2/\text{g}$ , further preferably between 70 and  $120 \text{ m}^2/\text{g}$ , more  
20 preferably between 70 and  $110 \text{ m}^2/\text{g}$  and most preferably between 70 and  $100 \text{ m}^2/\text{g}$ .

It is also preferred that the catalyst support has a hardness greater than/equal to 20 N, preferably greater than/equal to  
25 25 N, further preferably greater than/equal to 35 N and most preferably greater than/equal to 40 N. The hardness (indentation hardness) is to be determined as stated below.

By "natural sheet silicate", for which "phyllosilicate" is  
30 also used in the literature, is meant within the framework of the present invention untreated or treated silicate material from natural sources, in which  $\text{SiO}_4$  tetrahedra, which form the structural base unit of all silicates, are cross-linked with each other in layers of the general formula  $[\text{Si}_2\text{O}_5]^{2-}$ . These  
35 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

5 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 "sheet silicates" are to be found for example  
10 in "Lehrbuch der anorganischen Chemie", Hollemann Wiberg, de Gruyter, 102<sup>nd</sup> edition, 2007 (ISBN 978-3-11-017770-1) or in "Römpf Lexikon Chemie", 10<sup>th</sup> edition, Georg Thieme Verlag under "phyllosilicate". Typical treatments to which a natural sheet silicate is subjected before use as support material include  
15 for example a treatment with acids and/or calcining. A natural sheet silicate particularly preferred within the framework of the present invention is a bentonite. Admittedly, bentonites are not really natural sheet silicates, more a mixture of predominantly clay minerals containing sheet silicates. Thus  
20 in the present case, where the natural sheet silicate is a bentonite, it is to be understood that the natural sheet silicate is present in the catalyst support in the form of or as a constituent of a bentonite. It is particularly preferred that the bentonite is acid-treated and calcined.

25 It is preferred that the proportion of natural sheet silicate in the catalyst support is greater than/equal to 50 mass-%, preferably greater than/equal to 60 mass-%, preferably greater than/equal to 70 mass-%, further preferably greater than/equal  
30 to 80 mass-%, more preferably greater than/equal to 90 mass-% and most preferably greater than/equal to 93 mass-%, relative to the mass of the catalyst support.

It was found that the VAM selectivity of a VAM catalyst  
35 depends on the integral pore volume of the catalyst support according to the invention. It is therefore preferred that the catalyst support has an integral BJH pore volume of between 0.25 and 0.7 ml/g, preferably between 0.3 and 0.55 ml/g and by preference 0.35 to 0.5 ml/g.

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The integral pore volume of the catalyst support is determined according to the BJH method by means of nitrogen adsorption. The surface of the catalyst support and its integral pore volume are determined according to the BET or according to the BJH method. The BET surface area is determined according to the BET method according to DIN 66131; a publication of the BET method is also found in J. Am. Chem. Soc. 60, 309 (1938). In order to determine the surface and the integral pore volume of the catalyst support or the catalyst, the sample can be measured for example with a fully automatic nitrogen porosimeter from Micromeritics, type ASAP 2010, by means of which an adsorption and desorption isotherm is recorded. To determine the surface and the porosity of the catalyst support according to the BET theory, the data are evaluated according to DIN 66131. The pore volume is determined from the measurement data using the BJH method (E.P. Barret, L.G. Joiner, P.P. Haienda, J. Am. Chem. Soc. 73 (1951, 373)). Effects of capillary condensation are also taken into account when using this method. Pore volumes of specific pore size ranges are determined by totalling incremental pore volumes which are obtained from the evaluation of the adsorption isotherms according to BJH. The integral pore volume according to the BJH method relates to pores with a diameter of 1.7 to 300 nm.

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It is preferred according to a further preferred embodiment of the catalyst support according to the invention if at least 80%, preferably at least 85% and by preference at least 90%, of the integral pore volume of the catalyst support is formed by mesopores and macropores. This counteracts a reduced activity, effected by diffusion limitation, of the catalyst according to the invention, in particular with relatively thick Pd/Au shells. By "micropores", "mesopores" and "macropores" are meant in this case pores which have a

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5 diameter of less than 2 nm, a diameter of 2 to 50 nm and a diameter of greater than 50 nm respectively.

It is also preferred if the catalyst support has a bulk density of more than 0.3 g/ml, preferably more than 0.35 g/ml  
10 and particularly preferably a bulk density of between 0.35 and 0.6 g/ml.

It is further preferred if the natural sheet silicate contained in the support has an  $\text{SiO}_2$  content of at least 65  
15 mass-%, preferably at least 80 mass-% and by preference 95 to 99.5 mass-%. An adequate chemical resistance of the catalyst support according to the invention is thereby ensured.

In the gas-phase synthesis of VAM from acetic acid and ethene,  
20 a relatively low  $\text{Al}_2\text{O}_3$  content in the natural sheet silicate is scarcely disadvantageous, whereas with high  $\text{Al}_2\text{O}_3$  contents a marked reduction in indentation hardness must be expected. According to a preferred embodiment of the catalyst support according to the invention, the natural sheet silicate  
25 therefore contains less than 10 mass-%  $\text{Al}_2\text{O}_3$ , preferably 0.1 to 3 mass-% and by preference 0.3 to 1.0 mass-%, relative to the mass of the natural sheet silicate.

It is preferred according to a further preferred embodiment of  
30 the catalyst support according to the invention that the catalyst support is formed as a shaped body, for example as a sphere, cylinder, perforated cylinder, trilobe, ring, star or as a strand, preferably a ribbed strand or star-shaped strand, preferably as a sphere.

35 In addition, it is preferred that the catalyst support is formed as a sphere with a diameter greater than 2 mm, preferably with a diameter greater than 3 mm and by preference with a diameter greater than 4 mm.

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In addition, it is preferred that the maximum size of the catalyst support is smaller than 25 mm, preferably smaller than 10 mm.

- 10 It can also be preferred, in order to increase the activity of a VAM catalyst, that the catalyst support according to the invention 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  $\text{HfO}_2$  or  $\text{Fe}_2\text{O}_3$ . It is further  
15 preferred in this connection that the proportion of doping oxide in the catalyst support is between 0 and 20 mass-%, preferably 1.0 to 10 mass-% and by preference 3 to 8 mass-%. The doping can take place for example by surface doping, as is known from the state of the art, or the metal oxide/metal  
20 oxides can be incorporated into the matrix of the catalyst support, like the  $\text{ZrO}_2$  of the catalyst support according to the invention.

- In the catalyst support according to the invention, the  
25 zirconium oxide particles are preferably present in the form of microcrystallites and/or nanocrystallites, wherein the zirconium oxide is not necessarily present therein as pure  $\text{ZrO}_2$ , as it can also be present in the form of a mixed oxide.

- 30 It can be preferred that the  $\text{ZrO}_2$  particles themselves are doped with  $\text{Y}_2\text{O}_3$  or  $\text{HfO}_2$ .

- It can be provided according to a further preferred embodiment that the water absorbency of the catalyst support is 40 to  
35 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

5 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:

$$\begin{aligned} & (\text{amount weighed out (g)} - \text{amount weighed in (g)}) \times 10 = \text{water} \\ 10 & \text{ absorbency (\%)} \end{aligned}$$

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

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The catalyst support according to the invention can be prepared for example by grinding a pulverant (uncalcined) acid-treated bentonite as sheet silicate with a pulverant zirconium compound and water and then mixing thoroughly until  
20 homogeneous, shaping the resulting mixture, accompanied by compaction, into a shaped body by means of devices familiar to a person skilled in the art, such as for example extruders or tablet presses, and then calcining the unhardened shaped body to form a stable shaped body. The calcining is carried out at  
25 temperatures at which a solid structure is obtained and optionally the zirconium compound is converted into zirconium oxide  $\text{ZrO}_2$ . The size of the specific surface area (BET) of the catalyst support depends in particular on the quality of the (untreated) bentonite used, the acid-treatment method of the  
30 bentonite used, i.e. for example the nature and the quantity, relative to the bentonite, and the concentration of the inorganic acid used, the acid-treatment duration and temperature, on the moulding pressure and on the calcining duration and temperature and the calcining atmosphere.

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Acid-treated bentonites can be obtained by treating bentonites with strong acids such as for example sulphuric acid, phosphoric acid or hydrochloric acid. A definition, also valid within the framework of the present invention, of the term

5 bentonite is given in Römpp, Lexikon Chemie, 10<sup>th</sup> edition,  
Georg Thieme Verlag. Bentonites particularly preferred within  
the framework of the present invention are natural aluminium-  
containing sheet silicates which contain montmorillonite (as  
smectite) as main mineral. After the acid treatment, the  
10 bentonite is as a rule washed with water, dried and ground to  
a powder.

The process according to the invention for the preparation of  
a catalyst support, in particular a catalyst support according  
15 to the invention, comprises the steps:

- a) mixing a pulverant natural sheet silicate, in particular  
a pulverant acid-treated bentonite, with pulverant  
zirconium metal or a pulverant zirconium compound;  
20
- b) calcining the obtained mixture.

The preparation of a catalyst support according to the process  
according to the invention thus has only a single calcining  
25 step and is thus in this respect more cost-favourable than a  
surface-doping of a previously calcined support with zirconium  
oxide precursor compounds followed by a second calcining, or  
the application of zirconium dioxide or zirconium oxide  
precursor compounds as suspensions to previously calcined  
30 supports (WO2005065821) and their subsequent calcining,  
wherein this process actually also requires an additional  
binder, usually zirconyl acetate, in order to obtain an  
adequate strength of the catalyst support.

35 The calcining is preferably carried out at a temperature of  
400°C to 800°C, preferably at a temperature of 500°C to 700°C.

According to a preferred embodiment of the process according  
to the invention, the latter further comprises the step:

5 shaping a shaped body from the obtained mixture, preferably before carrying out step b).

The zirconium compound, provided it is not already zirconium oxide, is preferably converted into an oxide during the  
10 calcining.

The above-named process results in catalyst supports with a solid structure of sheet silicate and zirconium oxide particles sintered together, wherein the zirconium oxide  
15 particles are uniformly distributed in the structure of the particles.

In the above-named process, zirconium dioxide, zirconium hydroxide, zirconyl acetate or other zirconyl carboxylates,  
20 zirconium carbonate or zirconium oxycarbonate, zirconyl nitrate, zirconium naphthenate or ammonium zirconium carbonate, preferably zirconium hydroxide, are preferably used as pulverant zirconium compound. Where  $ZrO_2$  is used, it can be stabilized with  $Y_2O_3$  and/or  $HfO_2$ . A sintering of the  
25 constituents of the matrix of the catalyst support shaped body to form a stable structure of sheet silicate and optionally zirconium oxide particles is thereby guaranteed.

According to a further preferred embodiment of the process  
30 according to the invention, the process further comprises the step: treating the calcined mixture with an acid. A low acetic-acid solubility of the support when used in VAM synthesis is thereby achieved

35 As an alternative to a pulverant zirconium compound, colloidal  $ZrO_2$  in a solution or a corresponding sol can also be used.

5 According to a preferred embodiment of the process according to the invention, it is provided that the zirconium compound is converted into an oxide upon calcining.

According to a further preferred embodiment of the process  
10 according to the invention, it is preferred that zirconium oxide and/or zirconium hydroxide is used as zirconium compound.

It can also be provided that in step a)  $Y_2O_3$  and/or  $HfO_2$  is  
15 furthermore used.

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

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The present invention further relates to the use of the first, second and third catalyst support according to the invention in the preparation of a catalyst, in particular in the preparation of a shell catalyst.

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According to a preferred embodiment of the use according to the invention, it is provided that the shell catalyst is a shell catalyst for the preparation of vinyl acetate monomer, in particular a shell catalyst whose shell contains metal Pd and Au.  
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The present invention further relates to a shell catalyst for the preparation of VAM, comprising the first, second or third catalyst support according to the invention, whose shell  
35 contains metal Pd and Au.

Thus the present invention relates i.a. to a shell catalyst for the preparation of VAM, comprising a porous catalyst support shaped body with an outer shell which contains metal

5 Pd and Au, wherein the catalyst support shaped body, at least  
in the area of the outer shell, is formed of a matrix  
comprising a natural sheet silicate, in particular a matrix  
comprising an acid-treated, calcined bentonite, in which  
zirconium oxide ( $\text{ZrO}_2$ ) particles are contained uniformly,  
10 preferably homogeneously, distributed.

It was established that the advantages of the shell catalyst  
according to the invention, such as increased activity and  
selectivity, are already obtained if only the outer shell of  
15 the catalyst support, in which the noble metals Pd and Au are  
deposited, is formed of a matrix comprising a natural sheet  
silicate, in which zirconium oxide ( $\text{ZrO}_2$ ) particles are  
contained uniformly distributed. However, it is preferred  
according to the invention if the whole catalyst support of  
20 the catalyst according to the invention is formed from a  
matrix comprising a natural sheet silicate, in which zirconium  
oxide ( $\text{ZrO}_2$ ) particles are contained uniformly distributed.

According to a preferred embodiment of the catalyst according  
25 to the invention, it is provided that the zirconium oxide  
particles are contained in the catalyst support at a  
proportion of 1 to 25 mass-%, preferably at a proportion of 3  
to 20 mass-% and by preference at a proportion of 5 to 20  
mass-%, relative to the mass of the catalyst support.

30 According to a further preferred embodiment of the catalyst  
according to the invention, it is provided that the catalyst  
support has an acidity of between 1 and 150  $\mu\text{val/g}$ , preferably  
between 5 and 130  $\mu\text{val/g}$ , quite preferably between 10 and 100  
35  $\mu\text{val/g}$  and particularly preferably between 10 and 60  $\mu\text{val/g}$ .

According to a further preferred embodiment of the catalyst  
according to the invention, it is provided that the catalyst

5 support has an average pore diameter of 8 to 30 nm, preferably  
9 to 20 nm and by preference 10 to 15 nm.

According to a further preferred embodiment of the catalyst  
according to the invention, it is provided that the catalyst  
10 support has a surface of less than/equal to  $145 \text{ m}^2/\text{g}$ ,  
preferably less than  $142 \text{ m}^2/\text{g}$ , preferably less than  $140 \text{ m}^2/\text{g}$ ,  
further preferably less than  $137 \text{ m}^2/\text{g}$ , more preferably less  
than  $135 \text{ m}^2/\text{g}$ , still more preferably less than  $133 \text{ m}^2/\text{g}$  and  
particularly preferably less than  $130 \text{ m}^2/\text{g}$ .

15

According to a preferred embodiment of the catalyst according  
to the invention, it is provided that the catalyst support has  
a surface of  $60 \text{ m}^2/\text{g}$  to  $145 \text{ m}^2/\text{g}$ , preferably between  $65 \text{ m}^2/\text{g}$   
and  $140 \text{ m}^2/\text{g}$ , by preference between  $70 \text{ m}^2/\text{g}$  and  $130 \text{ m}^2/\text{g}$ ,  
20 further preferably between  $70 \text{ m}^2/\text{g}$  and  $120 \text{ m}^2/\text{g}$ , more  
preferably between  $70 \text{ m}^2/\text{g}$  and  $110 \text{ m}^2/\text{g}$  and most preferably  
between  $70 \text{ m}^2/\text{g}$  and  $100 \text{ m}^2/\text{g}$ .

In particular to keep the wear of the catalyst according to  
25 the invention within reasonable limits, the catalyst has a  
hardness greater than/equal to 20 N, preferably greater  
than/equal to 25 N, further preferably greater than/equal to  
35 N and most preferably greater than/equal to 40 N. The  
hardness is ascertained by means of an 8M tablet-hardness  
30 testing machine from Dr. Schleuniger Pharmatron AG,  
determining the average for 99 shell catalysts after drying of  
the catalyst at  $130^\circ\text{C}$  for 2h, wherein the apparatus settings  
are as follows:

|    |                                |           |
|----|--------------------------------|-----------|
| 35 | Hardness:                      | N         |
|    | Distance from the shaped body: | 5.00 mm   |
|    | Time delay:                    | 0.80 s    |
|    | Feed type:                     | 6 D       |
|    | Speed:                         | 0.60 mm/s |

5

The hardness of the catalyst can be influenced for example by varying certain parameters of the process for the preparation of the catalyst support, for example through the selection of the natural sheet silicate, the calcining duration and/or the calcining temperature of an unhardened shaped body shaped from the corresponding support mixture, or through specific additives such as for example methyl cellulose or magnesium stearate.

15 According to a further preferred embodiment of the catalyst according to the invention, it is provided that the proportion of natural sheet silicate, in particular acid-treated calcined bentonite, in the catalyst support is greater than/equal to 50 mass-%, preferably greater than/equal to 60 mass-%, preferably greater than/equal to 70 mass-%, further preferably greater than/equal to 80 mass-%, more preferably greater than/equal to 90 mass-% and most preferably greater than/equal to 93 mass-%, relative to the mass of the catalyst support.

25 According to a further preferred embodiment of the catalyst according to the invention, it is provided that the catalyst support has an integral BJH pore volume of between 0.25 and 0.7 ml/g, preferably between 0.3 and 0.55 ml/g and by preference between 0.35 and 0.5 ml/g.

30

According to a further preferred embodiment of the catalyst support according to the invention, it is provided that at least 80%, preferably at least 85% and by preference at least 90%, of the integral pore volume of the catalyst support is formed by mesopores and macropores.

35

According to a further preferred embodiment of the catalyst according to the invention, it is provided that the catalyst support has a bulk density of more than 0.3 g/ml, preferably

5 more than 0.35 g/ml and particularly preferably a bulk density of between 0.35 and 0.6 g/ml.

According to a further preferred embodiment of the catalyst according to the invention, it is provided that the natural  
10 sheet silicate contained in the support has an  $\text{SiO}_2$  content of at least 65 mass-%, preferably at least 80 mass-% and by preference 95 to 99.5 mass-%.

According to a further preferred embodiment of the catalyst  
15 according to the invention, it is provided that the natural sheet silicate contained in the support contains less than 10 mass-%  $\text{Al}_2\text{O}_3$ , preferably 0.1 to 3 mass-% and by preference 0.3 to 1.0 mass-%.

20 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, preferably as a sphere, cylinder, perforated cylinder, trilobe, ring, star or as a strand, preferably as a ribbed strand or star-shaped  
25 strand, preferably as a sphere.

According to a further preferred embodiment of the catalyst according to the invention, it is provided that the catalyst support is formed as a sphere with a diameter greater than 2  
30 mm, preferably with a diameter greater than 3 mm and by preference with a diameter greater than 4 mm.

In addition, it is preferred that the maximum size of the catalyst support is less than 25 mm, preferably less than 10  
35 mm.

According to a further preferred embodiment of the catalyst according to the invention, it is provided that the catalyst support is doped with at least one oxide of a metal, selected

5 from the group consisting of Hf, Ti, Nb, Ta, W, Mg, Re, Y and Fe, preferably with  $\text{HfO}_2$  or  $\text{Fe}_2\text{O}_3$ .

According to a further preferred embodiment of the catalyst according to the invention, it is preferred that the  
10 proportion of doping oxide in the catalyst support is between 0 and 20 mass-%, preferably 1.0 to 10 mass-% and by preference 3 to 8 mass-%.

In general, the smaller the thickness of the Pd/Au shell of  
15 the catalyst, the higher the VAM selectivity of the catalyst according to the invention. According to a further preferred embodiment of the catalyst according to the invention, the shell of the catalyst therefore has a thickness of less than/equal to 300  $\mu\text{m}$ , preferably less than/equal to 200  $\mu\text{m}$ ,  
20 preferably less than/equal to 150  $\mu\text{m}$ , further preferably less than/equal to 100  $\mu\text{m}$  and more preferably less than/equal to 80  $\mu\text{m}$ .

The thickness of the shell can be measured visually by means  
25 of a microscope. The area in which the noble metals are deposited appears black, while the areas free of noble metals appear white. As a rule, the boundary between areas containing noble metals and areas free of them is very sharp and can clearly be recognized visually. If the above-named boundary is  
30 not sharply defined and accordingly not clearly recognizable visually, the thickness of the shell corresponds to the thickness of a shell, measured starting from the outer surface of the catalyst support, which contains 95% of the noble metal deposited on the support.

35

It was likewise found that in the case of the catalyst according to the invention the Pd/Au shell can be formed with a relatively large thickness effecting a high activity of the

5 catalyst, without effecting a noteworthy reduction of the VAM selectivity of the catalyst according to the invention. According to another preferred embodiment of the catalyst according to the invention, the shell of the catalyst therefore has a thickness of between 200 and 2000  $\mu\text{m}$ ,  
10 preferably between 250 and 1800  $\mu\text{m}$ , by preference between 300 and 1500  $\mu\text{m}$  and further preferably between 400 and 1200  $\mu\text{m}$ .

In order to guarantee an adequate activity of the catalyst according to the invention, the proportion of Pd in the  
15 catalyst is 0.5 to 2.5 mass-%, preferably 0.6 to 2.3 mass-% and by preference 0.7 to 2 mass-%, relative to the mass of the catalyst support loaded with noble metal.

It can also be preferred if the catalyst according to the  
20 invention has a Pd content of 1 to 20 g/l, preferably 2 to 15 g/l and by preference 3 to 10 g/l.

In order to likewise guarantee an adequate activity and selectivity of the catalyst according to the invention, the  
25 Au/Pd atomic ratio of the catalyst is preferably between 0 and 1.2, preferably between 0.1 and 1, by preference between 0.3 and 0.9 and particularly preferably between 0.4 and 0.8.

It can also be preferred if the catalyst according to the  
30 invention has an Au content of 1 to 20 g/l, preferably 1.5 to 15 g/l and by preference 2 to 10 g/l.

In order to ensure a largely uniform activity of the catalyst according to the invention over the thickness of the Pd/Au  
35 shell, the noble-metal concentration should vary relatively little over the shell thickness. It is therefore preferred if, over an area of 90% of the shell thickness, the area being at a distance of 5% of the shell thickness from each of the outer

5 and inner shell limit, the profile of the noble-metal  
concentration of the catalyst varies from the average noble-  
metal concentration of this area by a maximum of  $\pm 20\%$ ,  
preferably by a maximum of  $\pm 15\%$  and by preference by a  
maximum of  $\pm 10\%$ . Such profiles can be obtained by the  
10 spraying, described below, of supports onto a fluid bed.

Chloride poisons the catalyst according to the invention and  
leads to a deactivation of same. According to a further  
preferred embodiment of the catalyst according to the  
15 invention, its chloride content is therefore less than/equal  
to 250 ppm, preferably less than/equal to 150 ppm.

The catalyst according to the invention preferably contains,  
in addition to zirconium oxide as further promoter, at least  
20 one alkali metal compound, preferably a potassium, sodium,  
caesium or rubidium compound, preferably a potassium compound.  
Suitable and particularly preferred potassium compounds  
include potassium acetate KOAc, potassium carbonate  $K_2CO_3$ ,  
potassium hydrogen carbonate  $KHCO_3$  and potassium hydroxide KOH  
25 and also all potassium compounds which change into K-acetate  
KOAc under the respective reaction conditions of VAM  
synthesis. The potassium compound can be deposited on the  
catalyst support both before and after the reduction of the  
metal components into the metals Pd and Au. According to a  
30 further preferred embodiment of the catalyst according to the  
invention, the catalyst comprises an alkali metal acetate,  
preferably potassium acetate. It is particularly preferred in  
order to ensure an adequate promoter activity if the alkali  
metal acetate content of the catalyst is 0.1 to 0.7 mol/l,  
35 preferably 0.3 to 0.5 mol/l. In the case of potassium acetate,  
the potassium acetate content of the catalyst according to the  
invention is preferably approximately 40 g/l.

5 According to a further preferred embodiment of the catalyst  
according to the invention, the alkali metal/Pd atomic ratio  
is between 1 and 12, preferably between 2 and 10 and  
particularly preferably between 4 and 9. Preferably, the  
smaller the surface of the catalyst support, the smaller the  
10 alkali metal/Pd atomic ratio.

The present invention also relates to a first process for the  
preparation of a catalyst, in particular a shell catalyst,  
comprising the steps:

- 15
- a) preparation of the first, second or third catalyst  
support according to the invention;
  - b) deposition of a solution of a Pd precursor compound onto  
20 the catalyst support;
  - c) deposition of a solution of an Au precursor compound onto  
the catalyst support;
  - d) conversion of the Pd component of the Pd precursor  
25 compound into the metal form; and
  - e) conversion of the Au component of the Au precursor  
compound into the metal form.

30

The outer ZrO<sub>2</sub>-doped shell of the catalyst support according to  
the invention has a thickness which corresponds at least to  
the thickness of the noble-metal shell to be deposited, for  
example a thickness of 500  $\mu\text{m}$ .

35

In principle, any Pd or Au compound by means of which a high  
degree of dispersion of the metals can be achieved can be used  
as Pd and Au precursor compound. By "degree of dispersion" is  
meant the ratio of the number of all the surface metal atoms

5 of all metal/alloy particles of a supported metal catalyst to  
 the total number of all the metal atoms of the metal/alloy  
 particles. In general it is preferred if the degree of  
 dispersion corresponds to a relatively high numerical value,  
 as in this case as many metal atoms as possible are freely  
 10 accessible for a catalytic reaction. This means that, given a  
 relatively high degree of dispersion of a supported metal  
 catalyst, a specific catalytic activity of same can be  
 achieved with a relatively small quantity of metal used.  
 According to a further preferred embodiment of the catalyst  
 15 according to the invention, the degree of dispersion of the  
 metal particles is 1 to 30%. The values of the degree of  
 dispersion are determined by means of CO adsorption according  
 to the corresponding DIN standard.

20 It can be preferred to select the Pd and Au precursor  
 compounds from the halides, in particular chlorides, oxides,  
 nitrates, nitrites, formates, propionates, oxalates, acetates,  
 hydroxides, hydrogen carbonates, amine complexes or organic  
 complexes, for example triphenylphosphine complexes or  
 25 acetylacetonate complexes, of these metals.

Examples of preferred Pd precursor compounds are water-soluble  
 Pd salts. According to a particularly preferred embodiment of  
 the process according to the invention, the Pd precursor  
 30 compound is selected from the group consisting of  
 $\text{Pd}(\text{NH}_3)_4(\text{OH})_2$ ,  $\text{Pd}(\text{NH}_3)_4(\text{OAc})_2$ ,  $\text{H}_2\text{PdCl}_4$ ,  $\text{Pd}(\text{NH}_3)_4(\text{HCO}_3)_2$ ,  
 $\text{Pd}(\text{NH}_3)_4(\text{HPO}_4)$ ,  $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ ,  $\text{Pd}(\text{NH}_3)_4$  oxalate, Pd oxalate,  
 $\text{Pd}(\text{NO}_3)_2$ ,  $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ ,  $\text{K}_2\text{Pd}(\text{OAc})_2(\text{OH})_2$ ,  $\text{Na}_2\text{Pd}(\text{OAc})_2(\text{OH})_2$ ,  
 $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ ,  $\text{K}_2\text{Pd}(\text{NO}_2)_4$ ,  $\text{Na}_2\text{Pd}(\text{NO}_2)_4$ ,  $\text{Pd}(\text{OAc})_2$ ,  $\text{K}_2\text{PdCl}_4$ ,  
 35  $(\text{NH}_4)_2\text{PdCl}_4$ ,  $\text{PdCl}_2$  and  $\text{Na}_2\text{PdCl}_4$ . Instead of  $\text{NH}_3$  the corresponding  
 complex salts can also be used with ethylenediamine or  
 ethanolamine as ligand. In addition to  $\text{Pd}(\text{OAc})_2$  other  
 carboxylates of palladium can also be used, preferably the

5 salts of the aliphatic monocarboxylic acids with 3 to 5 carbon atoms, for example the propionate or butyrate salt.

According to a further preferred embodiment of the process according to the invention, Pd nitrite precursor compounds can  
10 also be preferred. Preferred Pd nitrite precursor compounds are for example those which are obtained by dissolving  $\text{Pd}(\text{OAc})_2$  in an  $\text{NaNO}_2$  solution.

Examples of preferred Au precursor compounds are water-soluble  
15 Au salts. According to a particularly preferred embodiment of the process according to the invention, the Au precursor compound is selected from the group consisting of  $\text{KAuO}_2$ ,  $\text{HAuCl}_4$ ,  $\text{KAu}(\text{NO}_2)_4$ ,  $\text{AuCl}_3$ ,  $\text{KAuCl}_4$ ,  $\text{NaAuCl}_4$ ,  $\text{KAuCl}_4$ ,  $\text{KAu}(\text{OAc})_3(\text{OH})$ ,  $\text{HAu}(\text{NO}_3)_4$ ,  $\text{NaAuO}_2$ ,  $\text{NMe}_4\text{AuO}_2$ ,  $\text{RbAuO}_2$ ,  $\text{CsAuO}_2$ ,  $\text{NaAu}(\text{OAc})_3(\text{OH})$ ,  
20  $\text{RbAu}(\text{OAc})_3\text{OH}$ ,  $\text{CsAu}(\text{OAc})_3\text{OH}$ ,  $\text{NMe}_4\text{Au}(\text{OAc})_3\text{OH}$  and  $\text{Au}(\text{OAc})_3$ . It is recommended where appropriate to prepare fresh  $\text{Au}(\text{OAc})_3$  or  $\text{KAuO}_2$  each time by precipitating the oxide/hydroxide from a gold (III) hydroxide solution, washing and isolating the precipitate and taking up same in acetic acid or KOH.

25 All pure solvents or solvent mixtures in which the selected precursor compounds are soluble and which, after deposition onto the catalyst support, can be easily removed again from same by means of drying are suitable as solvents for the  
30 precursor compounds. Preferred solvents for metal acetates as precursor compounds are for example acetone or unsubstituted carboxylic acids, in particular acetic acid, and for the metal chlorides above all water or dilute hydrochloric acid.

35 If the precursor compounds are not sufficiently soluble in pure solvents such as acetone, acetic acid, water or dilute hydrochloric acid or mixtures thereof, other solvents or solvent additives can also be used as an alternative or in addition to the named solvents. Solvents which are inert and

5 miscible with acetic acid or water preferably come into  
consideration as other solvents in this case. Ketones, for  
example acetone or acetylacetone, furthermore ethers, for  
example tetrahydrofuran or dioxan, acetonitrile,  
dimethylformamide and solvents based on hydrocarbons such as  
10 for example benzene may be named as preferred solvents which  
are suitable for adding to acetic acid.

Ketones, for example acetone, or alcohols, for example ethanol  
or isopropanol or methoxyethanol, lyes, such as aqueous KOH or  
15 NaOH, or organic acids, such as acetic acid, formic acid,  
citric acid, tartaric acid, malic acid, glyoxylic acid,  
glycolic acid, oxalic acid, oxamic acid, glycine, pyruvic acid  
or lactic acid may be named as preferred solvents or additives  
which are suitable for adding to water.

20  
If chloride compounds are used as precursor compounds, it must  
be ensured that the chloride ions are reduced to a tolerable  
residual quantity before using the catalyst prepared according  
to the process according to invention, as chloride is a  
25 catalyst poison. For this, the catalyst support is as a rule  
washed with plenty of water after the fixing of the Pd and Au  
components of the Pd or Au precursor compound onto the  
catalyst support. In general, this happens either immediately  
after the fixing by hydroxide precipitation of the Pd and Au  
30 component by means of lye or after the reduction of the noble-  
metal components to the respective metal/alloy.

However, according to a preferred embodiment of the process  
according to the invention, chloride-free Pd and Au precursor  
35 compounds are used as well as chloride-free solvents to keep  
the chloride content in the catalyst as low as possible and  
avoid a laborious "washing free of chloride". The  
corresponding acetate, hydroxide or nitrite compounds are  
preferably used as precursor compounds, as they contaminate

5 the catalyst support with chloride to only a very small extent.

The deposition of the Pd and Au precursor compounds on the catalyst support in the area of an outer shell of the catalyst support can be achieved according to processes known per se. Thus the precursor solutions can be deposited by steeping, by dipping the support in the precursor solutions or steeping it according to the incipient wetness method. A base, for example caustic soda solution or potash lye, is then deposited on the catalyst support, whereby the noble-metal components are precipitated onto the support in the form of hydroxides. It is also possible for example to firstly steep the support in lye and then apply the precursor compounds to the thus-pretreated support.

20 According to a further preferred embodiment of the process according to the invention, it is therefore provided that the Pd and Au precursor compound is deposited on the catalyst support by steeping the catalyst support in the solution of the Pd precursor compound and in the solution of the Au precursor compound or in a solution which contains both the Pd and the Au precursor compound.

30 According to the state of the art, the active metals Pd and Au, starting from chloride compounds in the area of a shell of the support, are applied to same by means of steeping. However, this technique has reached its limits as regards minimum shell thicknesses and maximum Au loading. The shell thickness of the corresponding known VAM catalysts is at most approx. 100  $\mu\text{m}$  and it is not foreseen that even thinner shells can be obtained by means of steeping. In addition, higher Au loadings within the desired shell by means of steeping can be achieved only with difficulty, as the Au precursor compounds tend to diffuse from the shell into inner zones of the

5 catalyst support shaped body, which results in broad Au shells, areas of which contain very little Pd.

The active metals, or, put another way, their precursor compounds, can also be deposited on the support for example by  
10 means of so-called physical processes. For this, the support according to the invention can preferably be sprayed for example with a solution of the precursor compounds, wherein the catalyst support is moved in a coating drum into which hot air is blown, with the result that the solvent quickly  
15 evaporates.

But according to a further preferred embodiment of the process according to the invention, it is provided that the solution of the Pd precursor compound and the solution of the Au  
20 precursor compound are deposited onto the catalyst support by spraying the solutions onto a fluid bed or a fluidized bed of the catalyst support, preferably by means of an aerosol of the solutions. The shell thickness can thereby be continuously adjusted and optimized, for example up to a thickness of 2 mm.  
25 But even very thin noble-metal shells with a thickness of less than 100  $\mu\text{m}$  are thus possible.

It is preferred if the shaped bodies circulate elliptically or toroidally in the fluidized bed. To give an idea of how the  
30 shaped bodies move in such fluidized beds, it may be stated that in the case of "elliptical circulation" the catalyst support shaped bodies move in the fluidized bed in a vertical plane on an elliptical path, the size of the main and secondary axis changing. In the case of "toroidal circulation"  
35 the catalyst support shaped bodies move in the fluidized bed in the vertical plane on an elliptical path, the size of the main and secondary axis changing, and in the horizontal plane on an orbit, the size of the radius changing. On average, the shaped bodies move in the case of "elliptical circulation" in

- 5 the vertical plane on an elliptical path, in the case of  
"toroidal circulation" on a toroidal path, i.e., a shaped body  
covers the surface of a torus helically with vertical  
elliptical section.
- 10 The above-named embodiment of the process according to the  
invention is preferably carried out by means of a fluidized  
bed in a fluidized bed unit. It is particularly preferred if  
the unit contains a so-called controlled air-glide layer. For  
one thing, the catalyst support shaped bodies are thoroughly  
15 mixed by the controlled air-glide layer, wherein they  
simultaneously rotate about their own axis, whereby they are  
dried evenly by the process air. For another, due to the  
consequent orbital movement, effected by the controlled air-  
glide layer, of the shaped bodies the catalyst support shaped  
20 bodies pass through the spray procedure (application of the  
precursor compounds) at a virtually constant frequency. A  
largely uniform shell thickness of a treated batch of shaped  
bodies is thereby achieved. A further result is that the  
noble-metal concentration varies only slightly over a large  
25 area of the shell thickness, i.e. such that the noble-metal  
concentration describes a rectangular function over a large  
area of the shell thickness, whereby a uniform activity of the  
resulting catalyst is guaranteed over the thickness of the  
Pd/Au shell.
- 30
- Suitable coating drums, fluid bed units and fluidized bed  
units for carrying out the process according to the invention  
according to preferred embodiments are known in the state of  
the art and sold e.g. by Heinrich Brucks GmbH (Alfeld,  
35 Germany), ERWEK GmbH (Heusenstamm, Germany), Stechel  
(Germany), DRIAM Anlagenbau GmbH (Eriskirch, Germany), Glatt  
GmbH (Binzen, Germany), G.S. Divisione Verniciatura (Osteria,  
Italy), HOFER-Pharma Maschinen GmbH (Weil am Rhein, Germany),  
L. B. Bohle Maschinen + Verfahren GmbH (Enningerloh, Germany),

5 Lödige Maschinenbau GmbH (Paderborn, Germany), Manesty  
(Merseyside, United Kingdom), Vector Corporation (Marion, IA,  
USA), Aeromatic-Fielder AG (Bubendorf, Switzerland), GEA  
Process Engineering (Hampshire, United Kingdom), Fluid Air  
Inc. (Aurora, Illinois, USA), Heinen Systems GmbH (Varel,  
10 Germany), Hüttlin GmbH (Steinen, Germany), Umang Pharmatech  
Pvt. Ltd. (Marharashtra, India) and Innojet Technologies  
(Lörrach, Germany). Particularly preferred fluidized bed  
equipment is sold under the name Innojet® Aircoater or  
Innojet® Ventilus by Innojet Technologies.

15

According to a further preferred embodiment of the process  
according to the invention, the catalyst support is heated  
during deposition of the solutions, for example by means of  
heated process air. The drying-off speed of the deposited  
20 solutions of the noble-metal precursor compounds can be  
determined via the degree of heating of the catalyst supports.  
At relatively low temperatures the drying-off speed is for  
example relatively low, with the result that with a  
corresponding quantitative deposition, greater shell  
25 thicknesses can result because of the high diffusion of the  
precursor compounds that is caused by the presence of solvent.  
At relatively high temperatures the drying-off speed is for  
example relatively high, with the result that a solution of  
the precursor compounds coming into contact with the shaped  
30 body almost immediately dries off, which is why a solution  
deposited on the catalyst support cannot penetrate deep into  
the latter. At relatively high temperatures such relatively  
small shell thicknesses can thus be obtained with a high  
noble-metal loading. For example the catalyst support can be  
35 heated to a temperature of 40 to 80°C.

In the process described in the state of the art for the  
preparation of VAM shell catalysts based on Pd and Au,  
commercially available solutions of the precursor compounds

5 such as  $\text{Na}_2\text{PdCl}_4$ ,  $\text{NaAuCl}_4$  or  $\text{HAuCl}_4$  solutions are customarily  
used. In the more recent literature, as already stated  
previously, chloride-free Pd or Au precursor compounds such as  
for example  $\text{Pd}(\text{NH}_3)_4(\text{OH})_2$ ,  $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$  and  $\text{KAuO}_2$  are also  
used. These precursor compounds react base in solution, while  
10 the standard chloride, nitrate and acetate precursor compounds  
react acid in solution.

To deposit the precursor compounds onto the catalyst support,  
preferably aqueous  $\text{Na}_2\text{PdCl}_4$  and  $\text{NaAuCl}_3$  solutions are  
15 customarily used. These metal-salt solutions are normally  
applied to the support at room temperature and the metal  
components then fixed with NaOH as insoluble Pd or Au  
hydroxides. Then the loaded support is customarily washed free  
of chloride with water. In particular the Au fixing has  
20 disadvantages, such as long action times of the base in order  
to induce the precipitation of the stable Au tetrachloro  
complex, incomplete precipitation and concomitant inadequate  
Au retention.

25 According to a further preferred embodiment of the process  
according to the invention, the process comprises the steps:

- a) preparation of a first solution of a Pd and/or an Au  
precursor compound;
- 30 b) preparation of a second solution of a Pd and/or an Au  
precursor compound, wherein the first solution effects a  
precipitation of the noble-metal component(s) of the  
precursor compound(s) of the second solution and vice  
35 versa;
- c) deposition of the first solution and the second solution  
onto the catalyst support.

5 This embodiment of the process according to the invention uses two different precursor solutions, of which for example one contains a Pd and the other an Au precursor compound. Generally, one of the solutions preferably has a basic, and the other an acid pH. Generally, the solutions are deposited  
10 onto the catalyst supports by firstly impregnating the support with the first and then in a subsequent step with the second solution as described previously, for example by steeping. Upon deposition of the second solution the two solutions are then combined on the support, whereby the pH of the solutions  
15 changes and the Pd or Au component of the respective precursor compound is precipitated onto the support, without an auxiliary base customary in the state of the art, such as NaOH or KOH, having to be applied to the support.

20 The named embodiment of the process according to the invention is thus based on an impregnation of the catalyst support with the first solution of a Pd and/or Au precursor compound and the second solution of a Pd and/or Au precursor compound, wherein the two solutions are incompatible with each other,  
25 i.e., the first solution effects a precipitation of the noble-metal component(s) of the precursor compound(s) of the second solution and vice versa, with the result that in the contact zone of the two solutions both the pre-impregnated Pd /Au component(s) and the post-impregnated Pd /Au component(s)  
30 precipitate almost simultaneously and thus lead to an intimate thorough mixing of Pd/Au. Drying can optionally take place between the two impregnation steps.

Suitable aqueous solutions of Pd precursor compounds for the  
35 impregnation with incompatible solutions are listed by way of example in Table 1.

5 Table 1:

| Precursor compound                               | Character of the solution                             |
|--------------------------------------------------|-------------------------------------------------------|
| $\text{PdCl}_2$                                  | acid                                                  |
| $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$        | basic                                                 |
| $\text{Na}_2\text{PdCl}_4$                       | neutral                                               |
| $\text{Pd}(\text{NH}_3)_4(\text{OH})_2$          | basic                                                 |
| $\text{Pd}(\text{NO}_3)_2$                       | acid                                                  |
| $\text{K}_2\text{Pd}(\text{OAc})_2(\text{OH})_2$ | basic through dissolution of palladium acetate in KOH |

If, with regard to a premature Au reduction,  $\text{NH}_3$  were to have too strong a reductive effect, the corresponding diamine  
 10 complexes can also be used with ethylenediamine as ligand or the corresponding ethanol amine complexes instead of the palladium amine complexes.

Suitable aqueous solutions of Au precursor compounds for the  
 15 impregnation with incompatible solutions are listed by way of example in Table 2.

Table 2:

| Precursor compound                    | Character of the solution                                     |
|---------------------------------------|---------------------------------------------------------------|
| $\text{AuCl}_3$                       | acid                                                          |
| $\text{KAuO}_2$                       | basic through dissolution of $\text{Au}(\text{OH})_3$ in KOH  |
| $\text{NaAuCl}_4$                     | neutral                                                       |
| $\text{HAuCl}_4$                      | acid                                                          |
| $\text{KAu}(\text{OAc})_3(\text{OH})$ | basic through dissolution of $\text{Au}(\text{OAc})_3$ in KOH |
| $\text{HAu}(\text{NO}_3)_4$           | acid (stable in semi-concentrated $\text{HNO}_3$ )            |

- 5     Suitable combinations of incompatible solutions for the base-free precipitation of the noble-metal components are for example a  $\text{PdCl}_2$  and a  $\text{KAuO}_2$  solution; a  $\text{Pd}(\text{NO}_3)_2$  and a  $\text{KAuO}_2$  solution; a  $\text{Pd}(\text{NH}_3)_4(\text{OH})_2$  and an  $\text{AuCl}_3$  or  $\text{HAuCl}_4$  solution.
- 10    According to a further preferred embodiment of the process according to the invention, Pd can also be precipitated with incompatible Pd solutions and analogously Au with incompatible Au solutions, e.g. by bringing a  $\text{PdCl}_2$  solution into contact with a  $\text{Pd}(\text{NH}_3)_4(\text{OH})_2$  solution or a  $\text{HAuCl}_4$  with a  $\text{KAuO}_2$  solution.
- 15    In this way high Pd and/or Au contents can precipitate in the shell without having to use highly concentrated solutions.

According to a further embodiment of the process according to the invention, mixed solutions compatible with one another which are brought into contact with a solution incompatible with the mixed solution, can also be used for the noble-metal precipitation. An example of a mixed solution is a  $\text{PdCl}_2$  and  $\text{AuCl}_3$ -containing solution, the noble-metal components of which can be precipitated with a  $\text{KAuO}_2$  solution, or a  $\text{Pd}(\text{NH}_3)_4(\text{OH})_2$ - and  $\text{KAuO}_2$ -containing solution, the noble-metal components of which can be precipitated with a  $\text{PdCl}_2$ - and  $\text{HAuCl}_4$ -containing solution. A further example of a mixed solution is the  $\text{HAuCl}_4$  and  $\text{KAuO}_2$  pairing.

- 30    The impregnation with the incompatible solutions will preferably take place by means of steeping or by means of spray impregnation, wherein the incompatible solutions are for example sprayed simultaneously by one or more double nozzle(s) or simultaneously by means of two nozzles or nozzle groups or
- 35    sequentially by means of one or more nozzle(s).

Because of the rapid immobilization (fixing) of the metal components of the precursor compounds in the shell and the concomitant shortened Pd and Au diffusion, the impregnation

5 with the incompatible solutions can lead to thinner layers  
than the conventional use of solutions compatible with one  
another. By means of the incompatible solutions, high noble-  
metal contents in thin shells, improved metal retention, more  
rapid and more complete precipitation of the noble metals, the  
10 reduction of the disruptive residual Na content of the  
support, the simultaneous fixing of Pd and Au in only one  
fixing step, and also the absence of NaOH costs and NaOH  
handling and an avoidance of a mechanical weakening of the  
support through contact with excess NaOH can be achieved.

15 By means of the impregnation with incompatible solutions,  
greater noble-metal contents can be precipitated on the  
catalyst support through a single fixing step, which comprises  
just the deposition of two incompatible solutions, than is  
20 possible with standard base (NaOH) fixing.

In particular, high Au contents with an Au/Pd atomic ratio of  
0.6 and more, which is very desirable with regard to the  
increase in VAM selectivity, can be easily achieved by means  
of the principle of incompatible solutions.

25 According to a further preferred embodiment of the process  
according to the invention, it is provided that, once the Pd  
and/or the Au precursor compound has/have been deposited onto  
the catalyst supports for the fixing of the noble-metal  
30 component(s) of the precursor compound(s) onto the catalyst  
support, the catalyst support is subjected to a fixing step.  
The fixing step can comprise the treatment of the support with  
lye or acid, depending on whether the precursor compound is  
acid or basic, or a calcining of the support for converting  
35 the noble-metal component(s) into a hydroxide compound(s) or  
into an oxide is provided for. The fixing step can also be  
omitted and the noble-metal components directly reduced, e.g.  
by treatment with a gas phase with a reductive action, e.g.  
ethylene, etc., at increased temperatures of 20°C to 200°C.

5

It is likewise possible to prepare the catalyst according to the invention by means of a pulverant porous support material, comprising a mixture of particles of a natural sheet silicate, in particular an acid-treated (calcined or uncalcined)

10

bentonite, and zirconium oxide ( $\text{ZrO}_2$ ) particles, wherein the support material is loaded with a Pd and an Au precursor compound or with Pd and Au particles. The pre-treated support material can also be coated on as a secondary support e.g. in the form of a washcoat on a suitable primary support, for example a sphere of steatite or a KA-160 support from SÜD-Chemie AG, and then processed further into a catalyst by calcining and reduction.

15

20

Accordingly the invention relates to a further process for the preparation of a shell catalyst, in particular a shell catalyst according to the invention, comprising the steps

25

a) preparation of a pulverant porous support material, comprising a mixture of particles of a natural sheet silicate, in particular an acid-treated calcined bentonite, and zirconium oxide ( $\text{ZrO}_2$ ) particles, wherein the support material is loaded with a Pd and an Au precursor compound or with Pd and Au particles;

30

b) deposition of the support material from step a) onto a primary support in the form of a shell;

c) calcining of the loaded support structure from step b);

35

and

d) optional conversion of the Pd and the Au component of the Pd or Au precursor compound into the metal form.

- 5 Alternatively the named process can also be carried out by firstly depositing the noble-metal-free support material onto a support structure and only then application of the noble metals.
- 10 After loading with the precursor compounds or after fixing the noble-metal components, the support can be calcined to convert the noble-metal components into the corresponding oxides. Calcining preferably takes place at temperatures of less than 700°C, particularly preferably between 300-450°C accompanied
- 15 by the addition of air. Calcining time depends on the calcining temperature and is preferably chosen in the range from 0.5-6 hours. At a calcining temperature of approx. 400°C, the calcining time is preferably 1-2 hours. At a calcining temperature of approx. 300°C, the calcining time is preferably
- 20 up to 6 hours.

The noble-metal components are further reduced before the use of the catalyst, wherein the reduction can be carried out in situ, i.e. in the process reactor, or also ex situ, i.e. in a

25 special reduction reactor. Reduction in situ is preferably carried out with ethylene (5 vol.-%) in nitrogen at a temperature of approx. 150°C over a period of for example 5 hours. Reduction ex situ can be carried out for example with 5 vol.-% hydrogen, for example by means of forming gas, at

30 temperatures in the range of preferably 150-500°C, over a period of 5 hours.

Gaseous or vaporable reducing agents such as for example CO, NH<sub>3</sub>, formaldehyde, methanol and hydrocarbons can likewise be

35 used, wherein the gaseous reducing agents can also be diluted with inert gas, such as for example carbon dioxide, nitrogen or argon. An inert gas-diluted reducing agent is preferably used. Mixtures of hydrogen with nitrogen or argon, preferably

5 with a hydrogen content between 1 vol.-% and 15 vol.-%, are preferred.

The reduction of the noble metals can also be undertaken in the liquid phase, preferably by means of the reducing agents  
10 hydrazine, K-formate,  $H_2O_2$ , Na-hypophosphite, Na-formate, ammonium formate, formic acid, K-hypophosphite or hypophosphoric acid.

The quantity of reducing agent is preferably chosen such that  
15 during the treatment period at least the equivalent required for complete reduction of the noble-metal components is passed over the catalyst. Preferably, however, an excess of reducing agent is passed over the catalyst in order to guarantee a rapid and complete reduction.

20 The reduction is preferably pressureless, i.e. at an absolute pressure of approx. 1 bar. For the preparation of industrial quantities of catalyst according to the invention a rotary tube oven or fluid-bed reactor is preferably used in order to  
25 guarantee an even reduction of the catalyst.

The invention also relates to the use of the catalyst according to the invention as an oxidation catalyst, as a hydrogenation/dehydrogenation catalyst, as a catalyst in  
30 hydrogenating desulphurization, as a hydrodenitrification catalyst, as a hydrodeoxygenation catalyst or as a catalyst in the synthesis of alkenylalkanoates, in particular in the synthesis of vinyl acetate monomer (VAM), in particular in the gas-phase oxidation of ethylene and acetic acid to form vinyl  
35 acetate monomer.

The catalyst according to the invention is preferably used for the preparation of VAM. Generally this takes place by passing acetic acid, ethylene and oxygen or oxygen-containing gases

5 over the catalyst according to the invention at temperatures  
of 100-200°C, preferably 120-200°C, and at pressures of 1-25  
bar, preferably 1-20 bar, wherein non-reacted educts can be  
recycled. Expediently, the oxygen concentration is kept below  
10 vol.-%. Under certain circumstances, however, a dilution  
10 with inert gases such as nitrogen or carbon dioxide is also  
advantageous. Carbon dioxide is particularly suitable for  
dilution as it is formed in small quantities in the course of  
VAM synthesis. The formed vinyl acetate is isolated with the  
help of suitable methods, which are described for example in  
15 US 5,066,365 A.

The following embodiment examples serve, when viewed together  
with a comparison example, to explain the invention:

20 Example 1:

500 g of different acid-treated dried pulverant bentonite  
mixtures as sheet silicate based on natural bentonites with  
montmorillonite as main constituent were ground into an  
25 intimate mixture by means of a ball mill with up to 50 g  $\text{ZrO}_2$   
and 12 g methyl cellulose customary in the trade.

The resultant mixture was taken up with water and processed by  
means of a mixer into a dough from which spherical shaped  
30 bodies were prepared under pressure by means of a tablet  
press. For hardening, the spheres were calcined at a  
temperature of 600°C over a period of 5 h. The thus-obtainable  
shaped bodies have the characteristics listed in Table 3:

5 Table 3:

|    |                                |                                            |
|----|--------------------------------|--------------------------------------------|
|    | Geometric form                 | Sphere                                     |
|    | Diameter                       | 5 mm                                       |
| 10 | Moisture content               | <2.0 mass-%                                |
|    | Compressive strength           | >35 N                                      |
|    | Bulk density                   | 550 - 600 g l <sup>-1</sup>                |
|    | Water absorbency               | 55 - 70%                                   |
|    | Specific surface area (BET)    | 120-160 m <sup>2</sup> g <sup>-1</sup>     |
| 15 | SiO <sub>2</sub> content       | 80 to 90 mass-%                            |
|    | ZrO <sub>2</sub> content       | 3.7 to 9.5 mass-%                          |
|    | Other oxides                   | Residual mass in mass-%                    |
|    | Loss on ignition 1000°C        | <0.4 mass-%                                |
|    | Acidity                        | 10 to 100 µval/g                           |
| 20 | BJH pore volume N <sub>2</sub> | 0.3 - 0.45 cm <sup>3</sup> g <sup>-1</sup> |

225 g of the spheres prepared as above were packed in an Innojet Technologies (Lörrach, Germany) fluidized-bed device with the trade name Innojet® Aircoater and converted, by means of compressed air (6 bar) temperature-controlled at 80°C, into a fluidized-bed state in which the shaped bodies circulated toroidally, i.e. moved along a vertically aligned ellipsoid path and a horizontal circular path aligned perpendicular to this.

30

Once the shaped bodies were temperature-controlled at approx. 75°C, 300 ml of an aqueous noble-metal mixed solution containing 7.5 g Na<sub>2</sub>PdCl<sub>4</sub> (sodium tetrachloropalladate) customary in the trade and 4.6 g NaAuCl<sub>4</sub> (sodium tetrachloroaurate) customary in the trade were sprayed onto the fluidized bed of the shaped bodies over a period of 40 min.

35

5 After the impregnation of the catalyst support with the noble-metal mixed solution the support spheres were sprayed with a 0.05 molar NaOH solution in the fluidized-bed state under the above conditions over a period of 30 min. The NaOH was allowed to act on the shaped bodies for 16 h.

10

Following exposure to the action of the NaOH, the supports were washed with plenty of water in the fluidized-bed device, in order to very largely remove the alkali metal and chloride introduced into the support via the noble-metal compounds and NaOH.

15

After washing, the shaped bodies were dried in the fluidized-bed device at a temperature of 90 to 110°C.

20 After the shaped bodies were dried they were reduced to a Pd/Au shell catalyst with a gas mixture of ethylene (5 vol.-%) in nitrogen at a temperature of approx. 150°C in the fluidized-bed device.

25 The resulting shell catalyst contained approx. 1.2 mass-% Pd and had an Au/Pd atomic ratio of approx. 0.5 (determined by means of ICP (inductively coupled plasma)), a shell thickness of approx. 180  $\mu\text{m}$  and a hardness of 33 N.

30 The noble-metal concentration of the thus-prepared Pd/Au shell catalyst varied over an area of 90% of the shell thickness, the area being at a distance of 5% of the shell thickness from each of the outer and inner shell limit, from the average noble-metal concentration of this area by a maximum of +/- 10%. The noble-metal distribution was determined on a LEO 35 430VP scanning electron microscope, equipped with an energy-dispersive spectrometer from Bruker AXS. To measure the noble-metal concentration over the shell thickness, a catalyst sphere was cut in half, stuck to an aluminium sample holder

5 and then vapour-deposited with carbon. A nitrogen-free silicon drift detector (XFlash® 410) with an energy resolution of 125 eV for the manganese  $K_{\alpha}$  line was used as detector.

Example 2:

10 65 g support, prepared according to Example 1 with downstream acid treatment with the characteristics listed in Table 4:

Table 4:

|    |                                |                                       |
|----|--------------------------------|---------------------------------------|
|    | Geometric form                 | Sphere                                |
|    | Diameter                       | 5 mm                                  |
|    | Moisture content               | <2.0 mass-%                           |
| 20 | Compressive strength           | 50 N                                  |
|    | Bulk density                   | 585 g l <sup>-1</sup>                 |
|    | Water absorbency               | 61.3%                                 |
|    | Specific surface area (BET)    | 158 m <sup>2</sup> g <sup>-1</sup>    |
|    | SiO <sub>2</sub> content       | 83.3 mass-%                           |
| 25 | ZrO <sub>2</sub> content       | 5.2 mass-%                            |
|    | Other oxides                   | Residual mass in mass-%               |
|    | Loss on ignition 1000°C        | 3.6 mass-%                            |
|    | Acidity                        | 30 µval/g                             |
| 30 | BJH pore volume N <sub>2</sub> | 0.389 cm <sup>3</sup> g <sup>-1</sup> |

was impregnated, using the pore-filling method (incipient wetness method), in which a support is impregnated with a volume of solution corresponding to its pore volume, with 38.6 ml of an aqueous solution containing 1.568 g Na<sub>2</sub>PdCl<sub>4</sub> and 0.357 g HAuCl<sub>4</sub>. After the impregnation 89.14 g of a 0.35 molar NaOH solution was applied to the catalyst support and left to stand overnight at room temperature for 21 h. After decanting of the fixing solution the thus-prepared catalyst precursor was

5 reduced with 73.65 g of a 10%  $\text{NaH}_2\text{PO}_2$  solution for 2 h. After  
draining the reduction solution the catalyst was washed with  
distilled water for 8 h at room temperature, the water being  
constantly replaced (throughflow = 140 rpm) to remove Cl  
residues. The final value of the conductivity of the wash  
10 solution was 1.4  $\mu\text{S}$ .

The catalyst was then dried in the fluid bed at  $90^\circ\text{C}$  for 70  
min. The dried spheres were loaded with a mixture of 27.30 g 2  
molar KOAc solution and 13.59 g  $\text{H}_2\text{O}$  and left to stand for 1  
15 hour at room temperature. To conclude, drying takes place for  
70 min at  $90^\circ\text{C}$  in the fluid bed.

The theoretical loading of the supports with Pd is 0.8 wt.-%  
and 0.3 wt.-% Au; the experimental loading was 0.78 wt.-% Pd  
20 and 0.27 wt.-% Au (determined by means of ICP).

The shell thickness was 239  $\mu\text{m}$  (statistical average).

6 ml of a charge of catalyst spheres from Example 2 were  
25 impacted in a fixed-bed tubular reactor at a temperature of  
 $150^\circ\text{C}$  at 10 bar by a feed gas stream of 550 Nml/min composed  
of 15% HOAc, 6%  $\text{O}_2$ , 39%  $\text{C}_2\text{H}_4$  in  $\text{N}_2$  and the reactor output  
analyzed by means of gas chromatography.

30 The selectivity (of ethylene to VAM) is calculated according  
to the formula  $S(\text{C}_2\text{H}_4) = \text{mole VAM} / (\text{mole VAM} + \text{mole CO}_2/2)$ .  
The resultant space-time yield is given in g VAM/l catalyst/h.  
The rate of oxygen conversion is calculated according to (mole  
 $\text{O}_2$  in - mole  $\text{O}_2$  out)/mole  $\text{O}_2$  in.

35

The catalyst according to Example 2 according to the invention  
prepared by means of the catalyst support according to the  
invention displays a selectivity  $S(\text{C}_2\text{H}_4)$  of 92.4% and a space-

5 time yield (determined by means of gas chromatography) of 840  
g VAM / l catalyst / h at an oxygen conversion rate of 49.5%.

Comparison example:

10 100 g of a bentonite-containing support from SÜD-Chemie AG  
(Munich, Germany) with the trade name "KA-160" with the  
characteristics listed in Table 5:

Table 5:

|    |                                        |                                      |
|----|----------------------------------------|--------------------------------------|
|    | Geometric form                         | Sphere                               |
|    | Diameter                               | 5 mm                                 |
|    | Moisture content                       | <2.0 mass-%                          |
|    | Compressive strength                   | > 60 N                               |
| 20 | Bulk density                           | 554 g l <sup>-1</sup>                |
|    | Water absorbency                       | 62%                                  |
|    | Specific surface area (BET)            | 158 m <sup>2</sup> g <sup>-1</sup>   |
|    | SiO <sub>2</sub> content               | 93.2 mass-%                          |
|    | Al <sub>2</sub> O <sub>3</sub> content | 2.2 mass-%                           |
| 25 | Fe <sub>2</sub> O <sub>3</sub> content | 0.35 mass-%                          |
|    | TiO <sub>2</sub> content               | (total) < 1.5 mass-%                 |
|    | MgO content                            |                                      |
|    | CaO content                            |                                      |
| 30 | K <sub>2</sub> O content               |                                      |
|    | Na <sub>2</sub> O content              |                                      |
|    | Loss on ignition 1000°C                | <0.3 mass-%                          |
|    | Acidity                                | 53 µval/g                            |
| 35 | BJH pore volume N <sub>2</sub>         | 0.38 cm <sup>3</sup> g <sup>-1</sup> |

was impregnated with 62 ml of a 9.1% (relative to Zr) aqueous  
zirconyl nitrate solution according to the pore-filling method  
(incipient wetness method). The support was then dried at  
120°C over a period of 5 h and then calcined at 450°C in air

5 for 2 h. In this way a KA 160 support surface-doped with 5.2  
wt.-%  $\text{ZrO}_2$  was obtained.

Using the surface-doped KA 160 support, a catalyst was  
prepared analogously to Example 2.

10

The experimental loading of the supports with Pd was 0.77 wt.-%,  
that with Au 0.27 wt.-% (determined by means of ICP).

The shell thickness was 260  $\mu\text{m}$  (statistical average).

15

The performance of the catalyst of the comparison example was  
determined analogously to Example 2 and shows a selectivity  
 $S(\text{C}_2\text{H}_4)$  of 92.1% and a space-time yield (determined by gas  
chromatography) of 410 g VAM / l catalyst / h with an oxygen

20

conversion rate of 24.5%.

5

**Claims**

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1. Porous catalyst support, consisting of a material comprising a natural sheet silicate, wherein  $\text{ZrO}_2$  is contained distributed in the material.

2. Catalyst support according to claim 1, characterized in that the  $\text{ZrO}_2$  is contained uniformly distributed in the material.

3. Catalyst support according to claim 1 or 2, characterized in that the  $\text{ZrO}_2$  is present in particulate form.

4. Porous catalyst support, formed as a shaped body, with an outer shell, wherein the catalyst support, at least in the area of the outer shell, is formed from a matrix comprising a natural sheet silicate, in particular a matrix comprising an acid-treated calcined bentonite, in which zirconium oxide ( $\text{ZrO}_2$ ) particles are contained uniformly, preferably homogeneously, distributed.

5. Catalyst support according to claim 3 or 4, characterized in that the zirconium oxide particles are contained in the catalyst support at a proportion of 1 to 25 mass-%, preferably at a proportion of 3 to 20 mass-% and by preference at a proportion of 5 to 20 mass-% relative to the mass of the catalyst support.

6. Catalyst support according to one of claims 1 to 5, characterized in that the solubility of the catalyst support in acetic acid is less than 8 wt.-%, preferably less than 4 wt.-% and particularly preferably less than 2 wt.-%.

7. Catalyst support according to one of claims 1 to 6, characterized in that the natural sheet silicate comprises an acid-treated, calcined bentonite.

5

8. Catalyst support according to one of claims 1 to 7,  
characterized in that the catalyst support has an acidity of  
between 1 and 150  $\mu\text{val/g}$ , preferably between 5 and 130  
 $\mu\text{val/g}$ , by preference between 10 and 100  $\mu\text{val/g}$  and  
10 particularly preferably between 10 and 60  $\mu\text{val/g}$ .

9. Catalyst support according to one of claims 1 to 8,  
characterized in that the catalyst support has an average  
pore diameter of 8 to 30 nm, preferably 9 to 20 nm and by  
15 preference 10 to 15 nm.

10. Catalyst support according to one of claims 1 to 9,  
characterized in that the catalyst support has a surface  
less than/equal to 145  $\text{m}^2/\text{g}$ , preferably less than 142  $\text{m}^2/\text{g}$ ,  
20 by preference less than 140  $\text{m}^2/\text{g}$ , further preferably less  
than 137  $\text{m}^2/\text{g}$ , more preferably less than 135  $\text{m}^2/\text{g}$ , still  
more preferably less than 133  $\text{m}^2/\text{g}$  and particularly  
preferably less than 130  $\text{m}^2/\text{g}$ .

25 11. Catalyst support according to one of claims 1 to 10,  
characterized in that the catalyst support has a surface of  
145 to 60  $\text{m}^2/\text{g}$ , preferably between 140 and 65  $\text{m}^2/\text{g}$ , by  
preference between 135 and 70  $\text{m}^2/\text{g}$ , further preferably  
between 120 and 70  $\text{m}^2/\text{g}$ , more preferably between 110 and 70  
30  $\text{m}^2/\text{g}$  and most preferably between 100 and 70  $\text{m}^2/\text{g}$ .

12. Catalyst support according to one of claims 1 to 11,  
characterized in that the catalyst support has a hardness  
greater than/equal to 20 N, preferably greater than/equal to  
35 25 N, further preferably greater than/equal to 35 N and most  
preferably greater than/equal to 40 N.

13. Catalyst support according to one of claims 1 to 12,  
characterized in that the proportion of natural sheet

5       silicate, in particular acid-treated calcined bentonite, in  
the catalyst support is greater than/equal to 50 mass-%,  
preferably greater than/equal to 60 mass-%, by preference  
greater than/equal to 70 mass-%, further preferably greater  
than/equal to 80 mass-%, more preferably greater than/equal  
10       to 90 mass-% and most preferably greater than/equal to 93  
mass-%, relative to the mass of the catalyst support.

14. Catalyst support according to one of claims 1 to 13,  
characterized in that the catalyst support has an integral  
15       BJH pore volume of between 0.25 and 0.7 ml/g, preferably  
between 0.3 and 0.55 ml/g and by preference 0.35 to 0.5  
ml/g.

15. Catalyst support according to one of claims 1 to 14,  
20       characterized in that at least 80%, preferably at least 85%  
and by preference at least 90%, of the integral pore volume  
of the catalyst support is formed from mesopores and  
macropores.

25       16. Catalyst support according to one of claims 1 to 15,  
characterized in that the catalyst support has a bulk  
density of more than 0.3 g/ml, preferably more than 0.35  
g/ml and particularly preferably a bulk density of between  
0.35 and 0.6 g/ml.

30

17. Catalyst support according to one of claims 1 to 16,  
characterized in that the natural sheet silicate contained  
in the support has an SiO<sub>2</sub> content of at least 65 mass-%,  
preferably at least 80 mass-% and by preference 95 to 99.5  
35       mass-%.

18. Catalyst support according to one of claims 1 to 17,  
characterized in that the natural sheet silicate contained  
in the support contains less than 10 mass-% Al<sub>2</sub>O<sub>3</sub>,

- 5 preferably 0.1 to 3 mass-% and by preference 0.3 to 1.0 mass-%.
19. Catalyst support according to one of claims 1 to 18,  
characterized in that the catalyst support is formed as a  
10 shaped body, for example as a sphere, cylinder, perforated cylinder, trilobe, ring, star or as a strand, preferably as a ribbed strand or star-shaped strand, preferably as a sphere.
- 15 20. Catalyst support according to one of claims 1 to 19, characterized in that the catalyst support is formed as a sphere with a diameter greater than 2 mm, preferably with a diameter greater than 3 mm and by preference with a diameter greater than 4 mm.
- 20 21. Catalyst support according to one of claims 1 to 20, 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,  
25 preferably with  $\text{HfO}_2$  or  $\text{Fe}_2\text{O}_3$ .
22. Catalyst support according to claim 21, characterized in that the proportion of doping oxide in the catalyst support is between 0 and 20 mass-%, preferably 1.0 to 10 mass-% and  
30 by preference 3 to 8 mass-%.
23. Process for the preparation of a catalyst support, in particular of a catalyst support according to one of claims 1 to 22, comprising the following steps:
- 35 a) mixing a pulverant natural sheet silicate with pulverant zirconium metal or a pulverant zirconium compound;
- b) calcining the obtained mixture.

5

24. Process according to claim 23, characterized in that the process also comprises the step:

10       shaping a shaped body from the obtained mixture, preferably before carrying out step b).

25. Process according to claim 23 or 24, characterized in that zirconium dioxide, zirconium hydroxide, zirconyl acetate or other zirconyl carboxylates, zirconium carbonate or  
15       zirconium oxycarbonate, zirconyl nitrate, zirconium naphthenate or ammonium zirconium carbonate is used as pulverant zirconium compound.

26. Process according to one of claims 23 to 25, characterized  
20       in that the process also comprises the step: treating the calcined mixture with an acid.

27. Process according to one of claims 23 to 26, characterized  
25       in that the zirconium compound is converted into an oxide upon calcining.

28. Process according to one of claims 23 to 27, characterized  
in that zirconium oxide and/or zirconium hydroxide is used  
as zirconium compound.

30

29. Process according to one of claims 23 to 28, characterized in that in step a)  $Y_2O_3$  and/or  $HfO_2$  is furthermore used.

30. Use of a catalyst support according to one of claims 1 to  
35       22 in the preparation of a catalyst, in particular in the preparation of a shell catalyst.

31. Use according to claim 30, characterized in that the shell catalyst is a shell catalyst for the preparation of vinyl

5        acetate monomer, in particular a shell catalyst whose shell  
contains metal Pd and Au.

32.    Shell catalyst for the preparation of vinyl acetate  
monomer (VAM), comprising a catalyst support according to  
10       one of claims 1 to 22, whose outer shell contains metal Pd  
and Au.

33.    Shell catalyst for the preparation of vinyl acetate  
monomer (VAM), comprising a porous catalyst support shaped  
15       body with an outer shell which contains metal Pd and Au,  
wherein the catalyst support shaped body, at least in the  
area of the outer shell, is formed of a matrix comprising a  
natural sheet silicate, in particular a matrix comprising an  
acid-treated, calcined bentonite, in which zirconium oxide  
20       (ZrO<sub>2</sub>) particles are contained uniformly distributed.

34.    Catalyst according to claim 32 or 33, characterized in  
that the zirconium oxide particles are contained in the  
catalyst support at a proportion of 1 to 25 mass-%,  
25       preferably at a proportion of 3 to 20 mass-% and by  
preference at a proportion of 5 to 20 mass-% relative to the  
mass of the catalyst support.

35.    Catalyst according to one of claims 32 to 34,  
30       characterized in that the catalyst support has an acidity of  
between 1 and 150 µval/g, preferably between 5 and 130  
µval/g, by preference between 10 and 100 µval/g and  
particularly preferably between 10 and 60 µval/g.

35    36.    Catalyst support according to one of claims 32 to 35,  
characterized in that the catalyst support has an average  
pore diameter of 8 to 30 nm, preferably 9 to 20 nm and by  
preference 10 to 15 nm.

- 5 37. Catalyst according to one of claims 32 to 36,  
characterized in that the catalyst support has a surface of  
less than/equal to  $145 \text{ m}^2/\text{g}$ , preferably less than  $142 \text{ m}^2/\text{g}$ ,  
by preference less than  $140 \text{ m}^2/\text{g}$ , further preferably less  
than  $137 \text{ m}^2/\text{g}$ , more preferably less than  $135 \text{ m}^2/\text{g}$ , still  
10 more preferably less than  $133 \text{ m}^2/\text{g}$  and particularly  
preferably less than  $130 \text{ m}^2/\text{g}$ .
38. Catalyst according to one of claims 32 to 37,  
characterized in that the catalyst support has a surface of  
15  $60 \text{ m}^2/\text{g}$  to  $145 \text{ m}^2/\text{g}$ , preferably between  $65 \text{ m}^2/\text{g}$  and  $140 \text{ m}^2/\text{g}$ ,  
by preference between  $70 \text{ m}^2/\text{g}$  and  $130 \text{ m}^2/\text{g}$ , further  
preferably between  $70 \text{ m}^2/\text{g}$  and  $120 \text{ m}^2/\text{g}$ , more preferably  
between  $70 \text{ m}^2/\text{g}$  and  $110 \text{ m}^2/\text{g}$  and most preferably between  $70$   
 $\text{m}^2/\text{g}$  and  $100 \text{ m}^2/\text{g}$ .
- 20 39. Catalyst according to one of claims 32 to 38,  
characterized in that the catalyst has a hardness greater  
than/equal to 20 N, preferably greater than/equal to 25 N,  
further preferably greater than/equal to 35 N and most  
25 preferably greater than/equal to 40 N.
40. Catalyst according to one of claims 32 to 39,  
characterized in that the proportion of natural sheet  
silicate, in particular acid-treated calcined bentonite, in  
30 the catalyst support is greater than/equal to 50 mass-%,  
preferably greater than/equal to 60 mass-%, by preference  
greater than/equal to 70 mass-%, further preferably greater  
than/equal to 80 mass-%, more preferably greater than/equal  
to 90 mass-% and most preferably greater than/equal to 93  
35 mass-%, relative to the mass of the catalyst support.
41. Catalyst according to one of claims 32 to 40,  
characterized in that the catalyst support has an integral  
BJH pore volume of between 0.25 and 0.7 ml/g, preferably

5        between 0.3 and 0.55 ml/g and by preference 0.35 to 0.5  
ml/g.

42. Catalyst according to one of claims 32 to 41,  
characterized in that at least 80% of the integral pore  
10        volume of the catalyst support is formed from mesopores and  
macropores, preferably at least 85% and by preference at  
least 90%.

43. Catalyst according to one of claims 32 to 42,  
15        characterized in that the catalyst support has a bulk  
density of more than 0.3 g/ml, preferably more than 0.35  
g/ml and particularly preferably a bulk density of between  
0.35 and 0.6 g/ml.

20        44. Catalyst according to one of claims 32 to 43,  
characterized in that the natural sheet silicate contained  
in the support has an  $\text{SiO}_2$  content of at least 65 mass-%,  
preferably at least 80 mass-% and by preference 95 to 99.5  
mass-%.

25        45. Catalyst according to one of claims 32 to 44,  
characterized in that the natural sheet silicate contained  
in the support contains less than 10 mass-%  $\text{Al}_2\text{O}_3$ ,  
preferably 0.1 to 3 mass-% and by preference 0.3 to 1.0  
30        mass-%.

46. Catalyst according to one of claims 32 to 45,  
characterized in that the catalyst support is formed as a  
shaped body, for example as a sphere, cylinder, perforated  
35        cylinder, trilobe, ring, star or as a strand, preferably as  
a ribbed strand or star-shaped strand, preferably as a  
sphere.

- 5 47. Catalyst according to one of claims 32 to 46,  
characterized in that the catalyst support is formed as a  
sphere with a diameter greater than 2 mm, preferably with a  
diameter greater than 3 mm and by preference with a diameter  
greater than 4 mm.
- 10
48. Catalyst according to one of claims 32 to 47,  
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,  
15 preferably with  $\text{HfO}_2$  or  $\text{Fe}_2\text{O}_3$ .
49. Catalyst according to claim 48, characterized in that the  
proportion of doping oxide in the catalyst support is  
between 0 and 20 mass-%, preferably 1.0 to 10 mass-% and by  
20 preference 3 to 8 mass-%.
50. Catalyst according to one of claims 32 to 49,  
characterized in that the catalyst shell has a thickness of  
less than 300  $\mu\text{m}$ , preferably less than 200  $\mu\text{m}$ , by preference  
25 less than 150  $\mu\text{m}$ , further preferably less than 100  $\mu\text{m}$  and  
more preferably less than 80  $\mu\text{m}$ .
51. Catalyst according to one of claims 32 to 49,  
characterized in that the catalyst shell has a thickness of  
30 between 200 and 2000  $\mu\text{m}$ , preferably between 250 and 1800  $\mu\text{m}$ ,  
by preference between 300 and 1500  $\mu\text{m}$  and particularly  
preferably between 400 and 1200  $\mu\text{m}$ .
52. Catalyst according to one of claims 32 to 51,  
35 characterized in that the proportion of Pd in the catalyst  
is 0.5 to 2.5 mass-%, preferably 0.6 to 2.3 mass-% and by  
preference 0.7 to 2 mass-% relative to the mass of the  
catalyst support loaded with noble metal.

- 5 53. Catalyst according to one of claims 32 to 52,  
characterized in that the Au/Pd atomic ratio of the catalyst  
lies between 0 and 1.2, preferably between 0.1 and 1, by  
preference between 0.3 and 0.9 and particularly preferably  
between 0.4 and 0.8.
- 10
54. Catalyst according to one of claims 32 to 53,  
characterized in that the noble-metal concentration of the  
catalyst varies over an area of 90% of the shell thickness,  
the area being at a distance of 5% of the shell thickness  
15 from each of the outer and inner shell limit, from the  
average noble-metal concentration of this area by a maximum  
of +/- 20%, preferably by a maximum of +/- 15% and by  
preference by a maximum of +/- 10%.
- 20 55. Catalyst according to one of claims 32 to 54,  
characterized in that the catalyst has a chloride content of  
less than 250 ppm, preferably less than 150 ppm.
56. Catalyst according to one of claims 32 to 55,  
25 characterized in that the catalyst comprises an alkali metal  
acetate, preferably potassium acetate.
57. Catalyst according to claim 56, characterized in that the  
alkali metal acetate content of the catalyst is 0.1 to 0.7  
30 mol/l, preferably 0.3 to 0.5 mol/l.
58. Catalyst according to claim 56 or 57,  
characterized in that the alkali metal/Pd atomic ratio is  
between 1 and 12, preferably between 2 and 10 and by  
35 preference between 4 and 9.
59. Process for the preparation of a shell catalyst, in  
particular a shell catalyst according to one of claims 32 to  
58, comprising the steps

5

a) preparation of a catalyst support according to one of claims 1 to 22;

10

b) deposition of a solution of a Pd precursor compound onto the catalyst support;

c) deposition of a solution of an Au precursor compound onto the catalyst support;

15

d) conversion of the Pd component of the Pd precursor compound into the metal form;

and

20

e) conversion of the Au component of the Au precursor compound into the metal form.

25

60. Process according to claim 59, characterized in that the Pd and Au precursor compounds are selected from the halides, in particular chlorides, oxides, nitrates, nitrites, formates, propionates, oxalates, acetates, hydroxides, hydrogen carbonates, amine complexes or organic complexes, for example triphenylphosphine complexes or acetylacetonate complexes, of these metals.

30

35

61. Process according to claim 59 or 60, characterized in that the Pd precursor compound is selected from the group consisting of  $\text{Pd}(\text{NH}_3)_4(\text{OH})_2$ ,  $\text{Pd}(\text{NH}_3)_4(\text{OAc})_2$ ,  $\text{H}_2\text{PdCl}_4$ ,  $\text{Pd}(\text{NH}_3)_4(\text{HCO}_3)_2$ ,  $\text{Pd}(\text{NH}_3)_4(\text{HPO}_4)$ ,  $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ ,  $\text{Pd}(\text{NH}_3)_4$  oxalate,  $\text{Pd}(\text{NO}_3)_2$ ,  $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ ,  $\text{K}_2\text{Pd}(\text{OAc})_2(\text{OH})_2$ ,  $\text{Na}_2\text{Pd}(\text{OAc})_2(\text{OH})_2$ ,  $\text{Pd}(\text{NH}_3)_2(\text{NO}_2)_2$ ,  $\text{K}_2\text{Pd}(\text{NO}_2)_4$ ,  $\text{Na}_2\text{Pd}(\text{NO}_2)_4$ ,  $\text{Pd}(\text{OAc})_2$ ,  $\text{PdCl}_2$  and  $\text{Na}_2\text{PdCl}_4$ .

5 62. Process according to one of claims 59 to 61, characterized  
in that the Au precursor compound is selected from the group  
consisting of  $\text{KAuO}_2$ ,  $\text{HAuCl}_4$ ,  $\text{KAu}(\text{NO}_2)_4$ ,  $\text{AuCl}_3$ ,  $\text{NaAuCl}_4$ ,  
 $\text{KAuCl}_4$ ,  $\text{KAu}(\text{OAc})_3(\text{OH})$ ,  $\text{HAu}(\text{NO}_3)_4$ ,  $\text{NaAuO}_2$ ,  $\text{NMe}_4\text{AuO}_2$ ,  $\text{RbAuO}_2$ ,  
10  $\text{CsAuO}_2$ ,  $\text{NaAu}(\text{OAc})_3(\text{OH})$ ,  $\text{RbAu}(\text{OAc})_3\text{OH}$ ,  $\text{CsAu}(\text{OAc})_3\text{OH}$ ,  
 $\text{NMe}_4\text{Au}(\text{OAc})_3\text{OH}$  and  $\text{Au}(\text{OAc})_3$ .

63. Process according to one of claims 59 to 62, characterized  
in that the Pd and the Au precursor compound is deposited  
onto the catalyst support by steeping the catalyst support  
15 in the solution of the Pd precursor compound and in the  
solution of the Au precursor compound or in a solution which  
contains both the Pd and the Au precursor compound.

64. Process according to one of claims 59 to 62, characterized  
20 in that the Pd precursor compound and the Au precursor  
compound is deposited onto the catalyst support by spraying  
the solutions onto a fluid bed or a fluidized bed of the  
catalyst support, preferably by means of an aerosol of the  
solutions.

25 65. Process according to one of claims 59 to 64, characterized  
in that the catalyst support is heated during deposition of  
the solutions of the precursor compounds.

30 66. Process according to one of claims 59 to 65, characterized  
in that

a) a first solution of a Pd and/or an Au precursor compound  
is prepared;

35 b) a second solution of a Pd and/or an Au precursor compound  
is prepared, wherein the first solution effects a  
precipitation of the noble-metal component(s) of the

5 precursor compound(s) of the second solution and vice versa;

c) the first and the second solution are deposited onto the catalyst support.

10

67. Process according to claim 66, characterized in that the precursor compound of the first solution is acid and that of the second solution is basic.

15 68. Process according to one of claims 59 to 67, characterized in that the catalyst support is subjected to a fixing step once the Pd and/or the Au precursor compound has/have been deposited onto the catalyst support.

20 69. Process for the preparation of a shell catalyst, in particular a shell catalyst according to one of claims 32 to 58, comprising the steps

a) preparation of a pulverant porous support material, comprising a mixture of particles of a natural sheet silicate, in particular an acid-treated calcined bentonite, and zirconium oxide ( $\text{ZrO}_2$ ) particles, wherein the support material is loaded with a Pd and an Au precursor compound or with Pd and Au particles.

30

b) deposition of the support material onto a support structure in the form of a shell;

c) calcining of the loaded support structure from step b);

35

and

d) conversion of the Pd and the Au component of the Pd or Au precursor compound into the metal form.

5

70. Use of a catalyst according to one of claims 32 to 58 as  
an oxidation catalyst, as a hydrogenation/dehydrogenation  
catalyst, as a catalyst in hydrogenating desulphurization,  
as a hydrodeoxygenation catalyst, as a hydrodenitrification  
catalyst or as a catalyst in the synthesis of  
alkenylalkanoates, in particular in the synthesis of vinyl  
acetate monomer (VAM), in particular in the gas-phase  
oxidation of ethylene and acetic acid to form vinyl acetate  
monomer.

15