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Description

Surface impregnated catalyst, process for the production thereof, and use thereof for the preparation of vinyl acetate

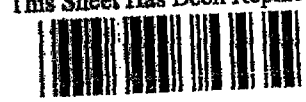
It is known that vinyl acetate can be prepared in the gas phase from ethylene, acetic acid and oxygen; the supported catalysts used for this synthesis comprise palladium and an alkali metal element, preferably potassium. Further additives used are cadmium, gold or barium.

In the Pd/K/Au catalysts both noble metals are generally applied in the form of an impregnated layer on the support; they are produced by impregnation and subsequent precipitation of the metal salts by means of alkaline compounds (US-A 4 048 096, US-A 3 775 342).

In Pd/K/Ba catalysts the metal salts are applied by impregnation, spraying on, vapor deposition, dipping or precipitation (EP-A-0 519 436). The same methods are known for Pd/K/Cd catalysts (US-A 4 902 823; US-A 3 393 199, US-A 4 668 819). Furthermore, the production of a Pd/K/Au or Pd/K/Cd surface impregnated catalyst is known, with a specific support material being washed with an acid prior to impregnation and being treated with a base after impregnation (EP-A-0 519 435).

The German Patent Application P 42 11 780.1 describes obtaining Pd/K/Au, Pd/K/Ba or Pd/K/Cd catalysts built up in the form of an impregnated layer by atomizing a solution of corresponding metal salts by means of ultrasound and then, in a limited amount and over a limited time applying this to the support particles and commencing the drying thereof in such a way that the catalytically active metal salts cannot penetrate into the core of

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the support particles, but only into an outer part having a greater or lesser thickness, the impregnated layer.

It has now been found that surface impregnated catalysts containing the specified elements are obtained much more simply by spraying a viscous solution of corresponding metal salts onto the support particles, instead of applying a solution after atomization into very fine droplets by means of ultrasound. The term "spray" here means that the liquid is applied in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets to the particles.

The invention provides a process for producing a surface impregnated catalyst comprising palladium, potassium and cadmium on porous support particles, which comprises spraying the support particles, while mixing intimately, once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa*s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

The invention also provides a surface impregnated catalyst produced in this manner, and also the use thereof for preparing vinyl acetate from ethylene, acetic acid and oxygen in the gas phase.

Preferably the solution volume in each spraying is from 15 to 60 %, in particular from 25 to 40 %, of the pore volume of the support particles to be impregnated with Pd, K and Cd salts.

The invention also provides a process for producing a surface impregnated catalyst comprising palladium, potassium and barium on porous support particles, which

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comprises spraying the support particles, while mixing intimately, once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

The invention also provides a surface impregnated catalyst produced in this manner, and also the use thereof for preparing vinyl acetate from ethylene, acetic acid and oxygen in the gas phase.

Preferably the solution volume in each spraying is from 15 to 50 %, in particular from 25 to 40 %, of the pore volume of the support particles to be impregnated with Pd, K and Ba salts.

The invention also provides a process for producing a surface impregnated catalyst comprising palladium, potassium and gold on porous support particles, which comprises spraying the support particles, while mixing intimately, once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

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Preferably the solution volume in each spraying is from 15 to 50 %, in particular from 25 to 40 %, of the pore volume of the support particles to be impregnated with Pd, K and Au salts.

Supports used are inert materials such as silicon dioxide, aluminum oxide or mixtures of these oxides in the form of spheres, pellets, rings, stars or other shaped bodies; the diameter, or the length and thickness, of the support particles is generally from 3 to 9 mm.

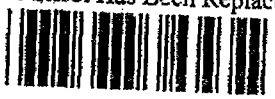
The surface area of the supports is, measured by the BET method, generally from 50 to 250 m^2/g; the pore volume is generally from 0.4 to 1.2 ml/g.

The metal contents of the finished catalysts are as follows:

The palladium content of the Pd/K/Cd and the Pd/K/Ba catalysts is generally from 0.6 to 3.5 % by weight, preferably from 0.8 to 3.0 % by weight, in particular from 1.0 to 2.5 % by weight. The palladium content of the Pd/K/Au catalysts is generally from 0.5 to 2.0 % by weight, preferably from 0.6 to 1.5 % by weight.
The potassium content of all three types of catalyst is generally from 0.5 to 4.0 % by weight, preferably from 1.5 to 3.0 % by weight.
The cadmium content of the Pd/K/Cd catalysts is generally from 0.1 to 2.5 % by weight, preferably from 0.4 to 2.0 % by weight.
The barium content of the Pd/K/Ba catalysts is generally from 0.1 to 2.0 % by weight, preferably from 0.2 to 1.0 % by weight.
The gold content of the Pd/K/Au catalysts is generally from 0.2 to 1.0 % by weight, preferably from 0.3 to 0.8 % by weight.

Suitable salts are all salts of palladium, cadmium,

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barium, gold and potassium which are soluble and contain no constituents, e.g. sulfur, which poison the catalyst; preference is given to the acetates and the chlorides. However, in the case of the chlorides, it must be ensured that the chloride ions are removed before the catalyst is used. This is achieved by washing the doped support, for example with water, after palladium and, if present, gold have been converted into an insoluble form, for instance by reduction and/or precipitation with hydroxides.

Suitable solvents are all compounds in which the selected salts are soluble and which after impregnation can easily be removed again by drying. Suitable solvents for the acetates are, in particular, unsubstituted carboxylic acids having from 2 to 10 carbon atoms, such as acetic acid, propionic acid, n- and iso-butyric acid and the various valeric acids. Owing to its physical properties and also for economic reasons, acetic acid is the preferred carboxylic acid. For the chlorides, water is particularly suitable. The additional use of a further solvent is advantageous if the salts are not sufficiently soluble in acetic acid or in water. Suitable additional solvents are those which are inert and miscible with acetic acid or water. Additives for acetic acid which may be mentioned are ketones such as acetone and acetylacetone, furthermore ethers such as tetrahydrofuran or dioxane, or else hydrocarbons such as benzene.

At least one salt of each of the three elements to be applied to the support particles (Pd/K/Cd, Pd/K/Ba, Pd/K/Au) has to be applied. A plurality of salts of one element can be applied, but in general exactly one salt of each of the three elements is applied.

The three elements to be applied in each case can be individually applied in the form of salt solutions, or otherwise in any combination. Use is preferably made of a single solution which contains all three elements to be applied in the form of salts. Particular preference is

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given to the use of a single solution which contains exactly one salt of each of the three elements to be applied.

If general reference is made hereinafter to "the solution of the salts" the same applies analogously to the case in which use is made, in order, of a plurality of solutions which each contain only a part of the total salts to be applied, with the individual parts adding up to the total amount of the salts which are to be applied to the support.

The solution of the salts is applied to the support particles by spraying these once or a plurality of times with this solution, with the total volume of the solution being used all at once or divided into two or more subvolumes. Subsequent to spraying, the support particles are immediately dried; in the case of spraying in order with a plurality of subvolumes, the support particles are immediately dried after each spraying.

The "immediate" drying here means that the drying of the sprayed particles has to be commenced promptly. It is here generally sufficient for the drying of the particles to be commenced at the latest after 1/2 hour after the completion of one spraying.

The dynamic viscosity of the solution is at least 0.003 Pa•s; the upper limit is determined by the solubility of the salts used in the selected solvent. Preferably the dynamic viscosity is from 0.005 to 0.009 Pa•s, in particular from 0.006 to 0.008 Pa•s.

The solution drops or solution jets are produced by driving the solution under an appropriate pressure through orifices of suitable size. The pressure is to be selected in such a way that the liquid impinges on the support particles in the form of drops or jets. Low pressures give drops, higher pressures give jets.

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The width of the orifices is, if drop formation is intended, to be selected in such a way that drops of an average diameter of at least 0.3 mm, preferably at least 0.6 mm, in particular at least 1 mm, are formed. The upper limit of the drop size is determined by the laws of physics, which do not allow the formation of drops of any size desired. This also determines the useful selection of the width of the orifices. Their width is to be selected so as to be at least that which gives drops of the abovementioned size, but naturally the width must not be so high that no drops at all are formed.

If the solution is to impinge on the support particles in the form of jets, which is preferred, an appropriate pressure must be used to drive the liquid through the orifice or the orifices of the spraying apparatus. The spraying apparatus can, for example, comprise one or more types of tube or a perforated plate. The width of the orifices of the spraying apparatus is, depending on pressure, to be selected so as to be at least that which gives liquid jets. In general, the width is at least 0.3 mm, preferably at least 0.5 mm. The upper limit of the suitable width is determined by the object of producing surface impregnated catalysts, i.e. supported catalysts in which the catalytically active metal salts have not penetrated into the support particles to the core, but only into the outer part, the impregnated layer. This is effected according to the invention, inter alia, by the solution volume in each spraying of the support particles being from 5 to 80 % of the pore volume of the particles. The width of the orifices and the number thereof is therefore to be selected in such a way as to give liquid jets which, on each spraying of the particles, apply the solution volume limited in the manner just mentioned to these.

During the spraying, the support particles must be intimately mixed, for example in a rotating flask or a mixing drum, to ensure a uniform impregnated layer

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thickness in all support particles. The rotation rate has, on the one hand, to be large enough to ensure good mixing, but on the other hand must not be so high that the support material is significantly abraded.

A suitable method of determining the desired distribution of the impregnated layer thicknesses comprises cutting open a representative number of support particles and measuring the impregnated layer thicknesses under a microscope. Here, preferably less than 5 % of the particles should have an impregnated layer thickness which deviates by more than 15 % from the average.

The solution of the salts should be at a temperature which is high enough to prevent precipitation of the salts during application to the support. However, the temperature should generally not be significantly above 70°C to prevent excessive evaporation of the solvent.

During the drying of the support impregnated with the solution of the active catalyst components, it is advisable to match the temperature to the type of metal salts used. In the case of the acetates, which are frequently used for the production of Pd/K/Cd or Pd/K/Ba catalysts, drying is preferably carried out at reduced pressure. The temperature should here generally be from 50 to 80°C, preferably from 50 to 70°C. Furthermore, it is generally advisable to carry out the drying in an inert gas stream, for example in a nitrogen or carbon dioxide stream. In the case of the Pd/K/Au catalysts, which are generally impregnated with the corresponding chlorides, the drying can, in contrast, be carried out in a hot air stream at from 100 to 150°C. The residual moisture content after drying should preferably be less than 6 % by weight for all three types of catalyst.

If a reduction of the palladium salt and, if applicable, of the gold salt is carried out, which is sometimes useful, this can be carried out using a gaseous reducing

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agent. The reduction in temperature is generally between 40 and 260°C, preferably between 70 and 200°C. In general it is advantageous to carry out the reduction using a reducing agent diluted with inert gas, which contains from 0.01 to 50 % by volume, preferably from 0.5 to 20 % by volume, of reducing agent. The inert gas used can be, for example, nitrogen, carbon dioxide, or a noble gas. Suitable reducing agents are, for example, hydrogen, methanol, formaldehyde, ethylene, propylene, isobutylene, butylene or other olefins. The amount of the reducing agent depends on the amount of palladium and, if applicable, on the amount of gold; the reduction equivalent should be at least 1 to 1.5 times the oxidation equivalent, but larger amounts of reducing agents do no harm. Such a reduction is carried out subsequent to drying.

The preparation of vinyl acetate is generally carried out by passing acetic acid, ethylene and oxygen or oxygen-containing gases over the finished catalyst at temperatures of from 100 to 220°C, preferably from 120 to 200°C and at pressures of from 1 to 25 bar, preferably from 1 to 20 bar, with unreacted components being able to be recirculated. The oxygen concentration is advantageously kept below 10 % by volume (based on the gas mixture free of acetic acid). However, dilution with inert gases such as nitrogen or carbon dioxide is sometimes also advantageous. Carbon dioxide is particularly suitable for the dilution, since it is formed in small amounts during the reaction.

The catalysts of the invention make it possible for the process to be carried out more selectively than when using catalysts in which the support particles are impregnated right into the core ("impregnated through"), or make possible an expansion of capacity. To achieve expansion of capacity, it is possible to keep the reaction conditions (e.g. pressure, temperature, throughput, oxygen concentration) unchanged in comparison with the known catalysts, and to prepare more vinyl acetate per

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reactor volume and time. This makes the work-up of the crude vinyl acetate obtained easier, since the vinyl acetate content in the exit gas from the reactor is higher, which leads further to a saving of energy in the work-up section. A suitable work-up is described, for example, in US-A 5 066 365.

If, in contrast, the plant capacity is kept constant, the reaction temperature can be lowered and thereby the reaction can be carried out more selectively at the same total output, which saves starting materials. Here the amount of carbon dioxide, which is formed as by-product and therefore has to be removed, and the loss of entrained ethylene associated with this removal are also smaller. In addition, this mode of operation prolongs the operating life of the catalyst.

The following examples illustrate the invention.

The catalyst support used was SiO_2 in the form of pellets having a diameter and a length of 6 mm in each case. The pellets had been pressed from ®Aerosil powder with the aid of magnesium stearate as binder in accordance with DE-A 3 912 504. The surface area of the support was 120 m^2/g, its pore volume was 0.784 ml/g and its bulk density was 500 g/l. The pore volume of 1 l of support was 392 ml.

Comparative Example 1a

1 l of silica support was impregnated at 60°C with a solution of 24.3 g of palladium acetate, 21.3 g of cadmium acetate and 23.8 g of potassium acetate in 392 ml of glacial acetic acid (solution volume = 100% of the pore volume of the support). The material was subsequently dried in a drying cabinet at 200 mbar under nitrogen to a residual acetic acid content of 6 % by weight; the drying temperature was 65°C. The finished catalyst contained 2.3 % by weight of Pd, 1.8 % by weight of Cd and 1.9 % by weight of K.

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A reaction tube having an internal diameter of 8 mm and a length of 1.5 m was charged with 50 ml of this catalyst. The gas to be reacted was then passed over the catalyst at a pressure of 8 bar (reactor inlet) and a catalyst temperature of 150°C. This gas comprised 27 % by volume of ethylene, 55 % by volume of nitrogen, 12 % by volume of acetic acid and 6 % by volume of oxygen. The results are shown in the table.

Comparative Example 1b

25.3 g of palladium acetate, 25 g of cadmium acetate and 25.3 g of potassium acetate were dissolved at 65°C in 137.2 ml of acetic acid (solution volume = 35 % of the pore volume) and the highly viscous solution was placed in a reservoir preheated to 65°C. 1 l of catalyst support was likewise heated to 65°C in a mixing drum able to be temperature controlled and were mixed at a rotation rate of 150 rpm. The impregnation solution was applied to the catalyst support by means of an ultrasound atomizer (100 kHz) over a period of one hour.

The material was subsequently dried as in Comparative Example 1a. The finished catalyst contained 2.3 % by weight of Pd, 1.8 % by weight of Cd and 1.9 % by weight of K. The impregnated layer thickness was 0.8 mm.

The catalyst was tested as in Comparative Example 1a and the results are shown in the table.

Comparative Example 2a

The catalyst was produced as in Comparative Example 1a, except that now 4.0 g of barium acetate were applied in place of cadmium acetate. The finished catalyst contained 2.3 % by weight of Pd, 0.4 % by weight of Ba and 1.9 % by weight of K.

The catalyst was tested as in Comparative Example 1a and the results are shown in the table.

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Comparative Example 2b

The catalyst was produced as in Comparative Example 1b, except that now 4.3 g of barium acetate were used in place of cadmium acetate. The finished catalyst contained 2.3 % by weight of Pd, 0.4 % by weight of Ba and 1.9 % by weight of K, the impregnated layer thickness was 0.8 mm.

The catalyst was tested as in Comparative Example 1a and the results are shown in the table.

Comparative Example 3a

1 l of silica support was, in accordance with EP-A-0 519 435, washed with 10 % strength hydrochloric acid and then with water to remove the binder interfering with formation of the impregnated layer and dried. The support was subsequently impregnated with a solution of 13.8 g of sodium chloropalladate and 4.0 g of tetrachloroauric acid in 392 ml of water. After drying with hot air at 150°C, 5.5 g of NaOH dissolved in 392 ml of water were added (to produce an impregnated layer by precipitation of palladium and gold). The material was subsequently stirred for 6 hours and allowed to stand for 16 hours at room temperature. After the support had been washed free of chloride with water and dried with hot air at 150°C, 35.1 g of potassium acetate in 392 ml of water were applied. After drying with hot air at 150°C the catalyst contained 1.0 % by weight of Pd, 0.4 % by weight of Au and 2.8 % by weight of K. The thickness of the impregnated layer produced by the treatment with sodium hydroxide solution was from 1.3 to 1.6 mm. The catalyst was tested in a Berty reactor at 152°C using a gas mixture of 8 % by volume of O_2, 37.5 % by volume of C_2H_4, 15.7 % by volume of HOAc and 38.8 % by volume of N_2; the results are shown in the table.

Comparative Example 3b

13.8 g of sodium chloropalladate and 4.0 g of tetrachloroauric acid were dissolved in 78.4 ml of water

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(solution volume = 20 % of the pore volume). The solution was applied at room temperature to 1 l of catalyst support by means of an ultrasound atomizer (100 kHz) over a period of one hour; the material was subsequently dried in a hot air stream at 150°C. To precipitate palladium and gold, a solution of 5.5 g of NaOH in 78.4 ml of water was then applied to the impregnated support using the ultrasound atomizer. It was then, in the same way as in Comparative Example 3a, washed free of chloride and dried. It was subsequently reduced with H_2, impregnated with 35.1 g of potassium acetate in 392 ml of water and dried using hot air at 150°C.

The finished catalyst contained 1.0 % by weight of Pd, 0.4 % by weight of Au and 2.8 % by weight of K; the impregnated layer thickness was 0.7 mm.

The catalyst was tested as in Comparative Example 3a and the results are shown in the table.

Example 1

25.3 g of palladium acetate, 25 g of cadmium acetate and 25.3 g of potassium acetate were dissolved at 65°C in 130.0 ml of acetic acid (solution volume = 33 % of the pore volume) and the highly viscous solution (7 mPa•s) was placed in a reservoir, preheated to 65°C. 1 l of the catalyst support was likewise heated to 65°C in a mixing drum able to be temperature controlled and mixed at a rotation rate of 10 rpm. The whole of the impregnation solution was sprayed onto the thus mixed catalyst support over a period of half an hour by means of a single tube having an internal diameter of 2 mm, i.e. it was impregnated using a single solution jet.

The material was subsequently dried as in Comparative Example 1a. The finished catalyst contained 2.3 % by weight of Pd, 1.8 % by weight of Cd and 1.9 % by weight of K. The impregnated layer thickness was 0.8 mm.

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The catalyst was tested as in Comparative Example 1a and the results are shown in the table.

Example 2

The catalyst was produced as in Example 1, except that now 4.3 g of barium acetate were used in place of cadmium acetate. The finished catalyst contained 2.3 % by weight of Pd, 0.4 % by weight of Ba and 1.9 % by weight of K, the impregnated layer thickness was 0.8 mm.

The catalyst was tested as in Comparative Example 1a and the results are shown in the table.

Example 3

13.8 g of sodium chloropalladate and 4.0 g of tetrachloroauric acid were dissolved in 78.4 ml of water (solution volume = 20 % of the pore volume). The solution was applied at room temperature over a period of half an hour as described in Example 1, in a single solution stream to 1 l of catalyst support; the material was subsequently dried in a hot air stream at 150°C. To precipitate palladium and gold, a solution of 5.5 g of NaOH in 78.4 ml of water was then sprayed onto the impregnated support over a period of half an hour by means of the tube having an internal diameter of 2 mm. It was then, in the same way as in Comparative Example 3a, washed free of chloride and dried. It was subsequently reduced with H_2, impregnated with 35.1 g of potassium acetate in 78.4 ml of water and dried using hot air at 150°C.

The finished catalyst contained 1.0 % by weight of Pd, 0.4 % by weight of Au and 2.8 % by weight of K; the impregnated layer thickness was 0.7 mm.

The catalyst was tested as in Comparative Example 3a and the results are shown in the table.

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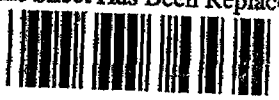
Example 4

10.120 kg of palladium acetate, 10.000 kg of cadmium acetate and 10.120 kg of potassium acetate were dissolved at 65°C in 52.0 l of acetic acid (solution volume = 33 % of the pore volume) and the highly viscous solution (7 mPa•s) was placed in a reservoir preheated to 65°C. 400 l of catalyst support were likewise heated to 65°C in a mixing drum able to be temperature controlled and were mixed at a rotation rate of 10 rpm. The whole of the impregnation solution was sprayed in the form of 140 solution jets onto the catalyst support over a period of half an hour. These solution jets were produced by driving the solution through 140 orifices in a perforated plate. The orifices had a width of 0.6 mm and were uniformly distributed over the support material.

The material was subsequently dried as in Comparative Example 1a. The finished catalyst contained 1.4 % by weight of Pd, 1.8 % by weight of Cd and 1.9 % by weight of K. The impregnated layer thickness was 0.5 mm.

The catalyst was tested as in Comparative Example 1a and the results are shown in the table.

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Table

	Output [g/lh]	Specific Output (*)	Vinyl acetate content (% by weight) of the condensed reactor exit gas	Selectivity [%]
Comparative Example 1a (Pd/K/Cd □)	813	70.7	25.7	94.3
Comparative Example 1b (Pd/K/Cd O)	915	79.6	33.0	96.3
Comparative Example 2a (Pd/K/Ba □)	827	71.9	25.9	92.8
Comparative Example 2b (Pd/K/Ba O)	917	79.7	33.1	95.7
Comparative Example 3a (Pd/K/Au #)	710	142.0	22.6	89.3
Comparative Example 3b (Pd/K/Au O)	740	148.0	24.2	90.0
Example 1 (Pd/K/Cd)	916	79.7	33.0	96.3
Example 2 (Pd/K/Ba)	918	79.8	33.1	95.7
Example 3 (Pd/K/Au)	742	148.4	24.2	90.0
Example 4 (Pd/K/Cd)	910	79.1	32.8	96.7

* Grams of vinyl acetate per gram of palladium per hour

□ Catalyst impregnated right through to the core of the support particles

O Surface impregnated catalyst produced by means of ultrasound spraying

\# Surface impregnated catalyst in accordance with EP-A-0 519 435 (precipitation with base)

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In Examples 1 to 4 of the invention, essentially the same results are achieved, therefore, as in Comparative Examples 1b, 2b and 3b in which the catalysts were produced by ultrasound spraying. Surprisingly, it is therefore not at all necessary for the production of a very high performance surface impregnated catalyst to divide the impregnation solution into extremely fine droplets by means of the complicated use of ultrasound, but the spraying of the invention using considerably larger drops or even liquid jets is sufficient.

As Comparative Examples 1a, 2a and 3a show, the performance data of impregnated-through catalysts or a surface impregnated catalyst in accordance with EP-A-0 519 435 are significantly worse.

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Claims

1. A process for producing a surface impregnated catalyst comprising palladium, potassium and cadmium on porous support particles, which comprises spraying the support particles, while mixing intimately, once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

2. The process as claimed in claim 1, wherein the solution volume in each spraying is from 15 to 60 % of the pore volume of the support particles.

3. A process for producing a surface impregnated catalyst comprising palladium, potassium and barium on porous support particles, which comprises spraying the support particles, while mixing intimately, once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

4. The process as claimed in claim 3, wherein the solution volume in each spraying is from 15 to 50 % of the pore volume of the support particles.

5. A process for producing a surface impregnated

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catalyst comprising palladium, potassium and gold on porous support particles, which comprises spraying the support particles, while mixing intimately, once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

6. The process as claimed in claim 5, wherein the solution volume in each spraying is from 15 to 50 % of the pore volume of the support particles.

7. The process as claimed in any one of claims 1 to 6, wherein the solution volume in each spraying is from 25 to 40 % of the pore volume of the support particles.

8. The process as claimed in any one of claims 1 to 7, wherein the dynamic viscosity of the solution is from 0.005 to 0.009 Pa•s.

9. The process as claimed in any one of claims 1 to 7, wherein the dynamic viscosity of the solution is from 0.006 to 0.008 Pa•s.

10. Use of the surface impregnated catalyst obtainable by the process claimed in any one of claims 1 to 9 for preparing vinyl acetate in the gas phase from ethylene, acetic acid and oxygen or oxygen-containing gases.

11. A surface impregnated catalyst comprising palladium, potassium and cadmium on porous support particles, obtainable by spraying the support particles, while

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mixing intimately, once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

12. A surface impregnated catalyst as claimed in claim 11, obtainable by the solution volume in each spraying being from 15 to 60 % of the pore volume of the support particles.

13. A surface impregnated catalyst comprising palladium, potassium and barium on porous support particles, obtainable by spraying the support particles, while mixing intimately, once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

14. A surface impregnated catalyst as claimed in claim 13, obtainable by the solution volume in each spraying being from 15 to 50 % of the pore volume of the support particles.

15. A surface impregnated catalyst comprising palladium, potassium and gold on porous support particles, obtainable by spraying the support particles, while mixing intimately, once or a plurality of times with

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at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

16. A surface impregnated catalyst as claimed in claim 15, obtainable by the solution volume in each spraying being from 15 to 50 % of the pore volume of the support particles.

17. A surface impregnated catalyst as claimed in any one of claims 11 to 16, obtainable by the solution volume in each spraying being from 25 to 40 % of the pore volume of the support particles.

18. A surface impregnated catalyst as claimed in any one of claims 11 to 17, obtainable by the dynamic viscosity of the solution being from 0.005 to 0.009 Pa•s.

19. A surface impregnated catalyst as claimed in any one of claims 11 to 17, obtainable by the dynamic viscosity of the solution being from 0.006 to 0.008 Pa•s.

What is claimed is:

1. A process for producing a surface impregnated catalyst comprising palladium, potassium and cadmium on porous support particles, which comprises spraying the support particles, while mixing intimately, once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

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2. The process as claimed in claim 1, wherein the solution volume in each spraying is from 15 to 60 % of the pore volume of the support particles.

3. The process as claimed in claim 1, wherein the dynamic viscosity of the solution is from 0.005 to 0.009 Pa•s.

4. A process for producing a surface impregnated catalyst comprising palladium, potassium and barium on porous support particles, which comprises spraying the support particles, while mixing intimately, once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

5. The process as claimed in claim 4, wherein the

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solution volume in each spraying is from 15 to 50 % of the pore volume of the support particles.

6. The process as claimed in claim 4, wherein the dynamic viscosity of the solution is from 0.005 to 0.009 Pa•s.

7. A process for producing a surface impregnated catalyst comprising palladium, potassium and gold on porous support particles, which comprises spraying the support particles, while mixing intimately, once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

8. The process as claimed in claim 7, wherein the solution volume in each spraying is from 15 to 50 % of the pore volume of the support particles.

9. The process as claimed in claim 7, wherein the dynamic viscosity of the solution is from 0.005 to 0.009 Pa•s.

10. A surface impregnated catalyst comprising palladium, potassium and cadmium on porous support particles, obtainable by spraying the support particles, while mixing intimately, once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s

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and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

11. A surface impregnated catalyst as claimed in claim 10, obtainable by the solution volume in each spraying being from 15 to 60 % of the pore volume of the support particles.

12. A surface impregnated catalyst as claimed in claim 10, obtainable by the dynamic viscosity of the solution being from 0.005 to 0.009 Pa•s.

13. A surface impregnated catalyst comprising palladium, potassium and barium on porous support particles, obtainable by spraying the support particles, while mixing intimately, once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

14. A surface impregnated catalyst as claimed in claim 13, obtainable by the solution volume in each spraying being from 15 to 50 % of the pore volume of the support particles.

15. A surface impregnated catalyst as claimed in claim 13, obtainable by the dynamic viscosity of the solution being from 0.005 to 0.009 Pa•s.

16. A surface impregnated catalyst comprising palladium, potassium and gold on porous support particles, obtainable by spraying the support particles, while

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mixing intimately, once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and drying the support particles immediately after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

17. A surface impregnated catalyst as claimed in claim 16, obtainable by the solution volume in each spraying being from 15 to 50 % of the pore volume of the support particles.

18. A surface impregnated catalyst as claimed in claim 16, obtainable by the dynamic viscosity of the solution being from 0.005 to 0.009 Pa•s.

19. A process for preparing vinyl acetate in the gas phase from ethylene, acetic acid and oxygen or oxygen-containing gases in the presence of a surface impregnated catalyst comprising palladium, potassium and cadmium on porous support particles, wherein the support particles are, while mixing intimately, sprayed once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and are immediately dried after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

20. The process as claimed in claim 19, wherein the solution volume in each spraying is from 15 to 60 % of the pore volume of the support particles.

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21. The process as claimed in claim 19, wherein the dynamic viscosity of the solution is from 0.005 to 0.009 Pa•s.

22. A process for preparing vinyl acetate in the gas phase from ethylene, acetic acid and oxygen or oxygen-containing gases in the presence of a surface impregnated catalyst comprising palladium, potassium and barium on porous support particles, wherein the support particles are, while mixing intimately, sprayed once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and are immediately dried after each spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

23. The process as claimed in claim 22, wherein the solution volume in each spraying is from 15 to 50 % of the pore volume of the support particles.

24. The process as claimed in claim 22, wherein the dynamic viscosity of the solution is from 0.005 to 0.009 Pa•s.

25. A process for preparing vinyl acetate in the gas phase from ethylene, acetic acid and oxygen or oxygen-containing gases in the presence of a surface impregnated catalyst comprising palladium, potassium and gold on porous support particles, wherein the support particles are, while mixing intimately, sprayed once or a plurality of times with at least one solution of at least one salt of each of the three elements in the form of drops having an average diameter of at least 0.3 mm or in the form of liquid jets and are immediately dried after each

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spraying, with the dynamic viscosity of the solution being at least 0.003 Pa•s and the solution volume in each spraying being from 5 to 80 % of the pore volume of the support particles.

26. The process as claimed in claim 25, wherein the solution volume in each spraying is from 15 to 50 % of the pore volume of the support particles.

27. The process as claimed in claim 25, wherein the dynamic viscosity of the solution is from 0.005 to 0.009 Pa•s.