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(54) PROCEDE DE PREPARATION D'UN CATALYSEUR DU TYPE A ENVELOPPE

(54) PROCESS FOR PREPARING A SHELL-TYPE CATALYST

(57) Procédé de préparation d'un catalyseur du type à enveloppe dans lequel une matière inorganique de support non poreuse, dont la surface spécifique, selon la méthode BET, est de 80 m^2/g, est pourvue d'une enveloppe extérieure constituée d'un catalyseur actif. Dans une première étape, une suspension d'au moins un composé de métal noble soluble dans l'eau et un composé de revêtement, dans une large mesure insoluble dans l'eau, sont séchés sur la matière de support. La matière de support obtenue revêtue d'une enveloppe extérieure est activée dans un courant de gaz réducteur. Grâce à ce procédé, il est possible de revêtir, simultanément et en une seule étape, une matière de support non poreuse au moyen d'une matière active et d'une matière de revêtement, afin de produire des vitesses spatiales plus élevées sans diminuer le taux de conversion pendant l'hydrogénation sélective de l'acétylène dans des courants gazeux en faisant appel au catalyseur du type à enveloppe produit.

(57) A process for preparing a shell-type catalyst in which a nonporous inorganic support material which has a BET surface area of less than 80 m^2/g is provided with a catalytically active outer shell. In an initial step, a suspension of at least one noble metal compound which is soluble in water and one coating compound, which is substantially insoluble in water, are dried onto the support material. The resulting support material coated with an outer shell is activated in a reducing gas stream. Using the process it is possible to coat a nonporous support material in a single step simultaneously with active and coating material to produce higher space velocities without a decrease in the rate of conversion during the selective hydrogenation of acetylene in gas streams by using the resulting shell-type catalyst.

ABSTRACT

A process for preparing a shell-type catalyst in which a nonporous inorganic support material which has a BET surface area of less than 80 m^2/g is provided with a catalytically active outer shell. In an initial step, a suspension of at least one noble metal compound which is soluble in water and one coating compound, which is substantially insoluble in water, are dried onto the support material. The resulting support material coated with an outer shell is activated in a reducing gas stream. Using the process it is possible to coat a nonporous support material in a single step simultaneously with active and coating material to produce higher space velocities without a decrease in the rate of conversion during the selective hydrogenation of acetylene in gas streams by using the resulting shell-type catalyst.

Process for preparing a shell-type catalyst

The present invention relates to a process for preparing a shell-type catalyst, and more particularly, the present invention relates to a process for preparing a shell-type catalyst in which a nonporous inorganic support material with a low BET surface area of less than 80 m^2/g, is provided with a catalytically active outer shell.

Metals, preferably noble metals, are used in many industrial processes for catalytic purposes, in elemental form or as oxides, bonded to a support. Porous or nonporous materials may be used as catalyst supports.

When impregnating support materials with aqueous metal salt solutions and then reducing the salt, the metal may be deposited onto the support in the form of an outer shell which completely encases the support. It is known that these shell-type catalysts are particularly suitable, *inter alia,* for selective hydrogenations and for oxidation reactions using oxygen in the gas phase.

One area of application of particular interest relates to the selective hydrogenation of acetylene, in particular the purification of a hydrogen chloride gas stream within the oxychlorination process circuit for preparing vinyl chloride.

Vinyl chloride is prepared, either purely thermally or in the presence of catalysts at elevated temperature, from 1,2-dichloroethane with the elimination of hydrogen chloride. After isolating most of the vinyl chloride, a hydrogen chloride gas is produced which generally contains up to 3,000 ppm v/v of acetylene. Before returning this hydrogen chloride to the oxychlorination process, as much as possible of the unwanted acetylene has to be removed from the gas mixture, in an intermediate stage. This takes place by catalytic hydrogenation, wherein the essential requirement is removal of as much of the acetylene as possible (residual acetylene concentration less than 30 ppm v/v) by selective hydrogenation of the acetylene to give ethylene which can be used in the oxychlorination process.

The process conditions for purification of the hydrogen chloride gas stream mentioned above are described in detail in EP 0052271 B1 and United States Patent No. 4,388,278. Hydrogenation is generally performed with a clear excess of hydrogen in the temperature range of 120°C to 180°C, and in a pressure range of from 6 bar to 20 bar absolute.

Fixed bed catalysts are used to purify the hydrogen chloride gas stream by selective hydrogenation of the acetylene contained therein. These are preferably palladium-containing catalysts. Catalyst formulations on aluminium oxide have been disclosed for this use, but they are restricted with regard to performance potential, selectivity and durability.

In patent DE 30 37 047 C2, a fixed bed catalyst is described where the catalyst is prepared by impregnating silicon carbide as support material with a solution of a palladium salt, and then drying and reducing the palladium salt with hydrogen. This catalyst is prepared on a relatively expensive support material.

EP-0 576 944 A1 discloses shell-type catalysts prepared by depositing an alloy by PVD (physical vapour deposition) and/or chemical vapour deposition (CVD) on a moulded article.

Nonporous moulded articles made of glass, quartz glass, ceramic, titanium dioxide, zirconium dioxide, aluminium oxide, aluminium silicates, borates, steatite, magnesium silicate, silicon dioxide, silicates, metal, carbon, e.g. graphite, or mixtures of these materials may be used as supports. The alloy layer deposited on the moulded article contains at least one metal which is preferably very easily oxidised, such as silicon, aluminium, zirconium or titanium. The thickness of the layer is within the range 100 nm to 50 µm.

Finally, EP 0 755 718 A1 describes a process for preparing loaded nonporous support materials. The nonporous inorganic support materials may be coated with metal and/or metal oxide in an abrasion-resistant manner by applying highly dilute, aqueous solutions of at least one metal compound to the heated moulded article in such a way that the water evaporates immediately and then optionally calcining at an elevated temperature.

DE 32 00 483 A1 discloses a process for preparing silica-containing moulded articles in which a mixture of soluble and insoluble silicas are applied to an inorganic substrate. The resulting moulded articles may be used as supports for a variety of catalytic materials.

A catalyst for use in the case of hydrogen chloride gas purification by selective hydrogenation of acetylene has also been described, silicon dioxide being used as the support material (Chem.-Ing.-Tech. 59 (1987) No. 8, pp 645-647). This catalyst is, like the other formulations, limited with regard to its performance (space velocity characteristics).

Having regard to the prior art, an object of one embodiment of the invention is to provide a process for preparing a shell-type catalyst which enables the production in a simple manner of a catalyst for the application mentioned even at elevated space velocities (GHSV greater than 3000/h).

In accordance with one aspect of the one embodiment of the present invention there is provided a process for preparing a shell-type catalyst in which a nonporous inorganic support material having a BET surface area of less than 80 m^2/g is provided with a catalytically active outer shell, comprising:
providing a suspension of at least one noble metal compound which is soluble in water;
providing a coating compound substantially insoluble in water;
drying the suspension and the coating compound onto the support material;
coating a dried and coated support material with an outer shell; and
activating the support coated with the outer shell with a reducing gas.

The result is the preparation of a shell-type catalyst in which a nonporous inorganic support material, having a BET surface area of less than 80 m^2/g, is provided with a catalytically active outer shell. Initially, in a first step, a suspension of at least one water soluble noble metal compound and one coating compound which is substantially insoluble in water is dried onto the support material. In a second step, the resulting support material coated with an outer shell is activated in a reducing gas stream which results in producing, in a simple and not readily predictable manner, a product which corresponds to the previously mentioned objectives.

Surprisingly, using the process according to the invention, it is possible to coat a nonporous support material with active material and coating material at the same time in a single working process. This advantageous surface-active structure is obtainable by practicing the invention in a surprisingly simple manner.

The method of preparation according to the invention and the method of preparation disclosed in the previously published prior art for shell-type catalysts differ considerably. Thus, in EP 0 576 944, the deposition of a noble metal alloy is achieved by means of PVD or CVD in a high vacuum. These processes require costly equipment to effect desirable results.

In EP 0 755 718 A1 water-soluble metal compounds or metal salts, in which the metal concentration is restricted to 2 wt.%, are deposited onto support materials in a moving bed. There is an additional condition that immediate evaporation of the solvent water has to be ensured. In contrast to the process disclosed in EP 0 755 718, according to the present invention suspensions consisting of a water-soluble material and a substantially water-insoluble material are dried onto a nonporous support. The shell-type catalyst produced in this way may have a different structure, but the coated shell-type catalyst is always particularly simple to produce.

Nonporous inorganic support materials which may be coated within the context of the process according to the invention include in particular granulates, moulded articles or ceramic supports. Good results can be obtained with ceramic supports, in particular those based on aluminium oxide and/or silicates. Furthermore, the very wide variety of aluminium silicates, aluminium oxide, silicon carbide with added aluminium oxide and silicon dioxide, zirconium dioxide with and without added aluminium oxide and silicon dioxide, titanium dioxide with and without aluminium oxide and silicon dioxide, for example corundum, feldspar, mica, steatite, ceramic stoneware, glass, quartz etc. are beneficial.

In one embodiment, the process of the invention is characterised in that moulded articles made of glass, quartz, ceramic, silicon dioxide, aluminium oxide, graphite, moulded carbon, metal or steatite are used as support materials. Of these, moulded articles based on SiO_2 and/or Al_2O_3 are again of particular interest.

SiO_2 granulates with different granular sizes may also be mentioned as being of great interest as support materials in the process according to the invention.

The materials which can be used as supports for the shell-type catalyst prepared according to the invention may have a very wide variety of external shapes. As an example, they may be granules, moulded articles in the form of spheres, tablets and/or strands. As a variation, of the process, support materials in the form of hollow extrudates, solid extrudates, spheres, granules, tablets and/or strands are used. The support materials may also be used as an extrudate, as a hollow extrudate, as tubular sections, as rings or in the shape of discs.

In a further variation, granular materials are coated using the process set forth herein. Good to very good shell-type preparations have also been obtained in particular on ceramic materials (aluminosilicates).

Depending on the ultimate purpose of the shell-type catalysts, support materials capable of rolling may be of advantage. In this case spheres are particularly preferred.

The particle diameter of the support materials to be coated is not critical and may vary over a wide range. The supports preferably have particle diameters in the range from 0.5 to 50 mm. The range from 1 to 20 mm is most desirable.

In one variant the range of greater than 1 mm is quite preferred. Occasionally, particle diameters of less than 0.5 mm may also be of use, depending on the ultimate purpose.

The BET surface area of the inorganic support materials to be provided with an outer shell according to the invention is less than 80 m^2/g, which means that the support is nonporous. It is expedient that support materials with a

BET surface area of less than 30 m^2/g, preferably less than 10 m^2/g are used.

In addition to the BET surface area of the support material, the pore volume is of some significance in a particularly expedient variant of the invention. Thus one advantageous variant of the process in the invention is characterised in that support materials with a pore volume of less than 0.5 ml/g are used. Support materials with a pore volume of less than 0.1 ml/g are particularly expediently used.

One particularly expedient version of the nonporous inorganic support materials in the shell-type catalysts being prepared according to the invention has a very low concentration of Fe_2O_3. Fe_2O_3 concentrations of less than 0.5 wt.%, with respect to the weight of support material, are preferred.

When preparing a shell-type catalyst according to the invention, in a first step a noble metal compound which is soluble in water is dried onto the support material together with the coating material. "Water-soluble" in the context of the invention refers to compounds which can be dissolved in water at 30°C at a concentration, calculated as metal, of 0.01 preferably 0.05 wt.%.

Noble metal compounds which are soluble in water include preferably water-soluble compounds of Ru, Rh, Pd, Ag, Os, Ir, Pt and/or Au.

Oxides, hydroxides, carbonates, halides, nitrates, salts of organic acids and/or other common complex compounds which contain noble metal ions may be used. Soluble noble metal compounds may also include acids, such as hexachloropalladium solutions. Noble metal salt solutions which contain palladium are preferably used according to the invention. Palladium salt solutions such as palladium chloride and palladium nitrate solutions are particularly preferred.

Basically the noble metal concentration of the soluble noble metal compounds being used in the process in the invention may take on any value and is governed to some extent by availability, but it is quite particularly stressed that the process of the invention is characterised in a particularly expedient variant by the water-soluble noble metal compound being used as an aqueous solution containing the noble metal compound, calculated as metal, at a concentration of greater than 1 wt.%. Noble metal solutions with a concentration of greater than 5% noble metal, calculated as metal are used in particular. Solutions which have a concentration of less than 1 wt.% of noble metal have to be used in unusually large amounts. This results in an extended drying time in order to achieve the corresponding noble metal concentration in the catalyst shell. As already mentioned, the soluble noble metal compounds which are used according to the invention are preferably those which can dissolve in water at 30°C at a concentration, with respect to metal, of at least 0.01 wt.%.

In contrast, the coating compounds which are substantially insoluble in water and dried onto the support material at the same time as the water-soluble noble metal compound are those compounds which, in a preferred embodiment, can dissolve in water at 30°C at a concentration, calculated as metal, of less than 4 wt.%.

These coating compounds have poor solubility in water, which results in the production of a suspension applied in the first step.

Finely divided inorganic compounds of the metal oxide type are included among coating materials which may be used according to the invention. SiO_2, Al_2O_3, TiO_2 and/or ZrO_2 include suitable examples; SiO_2 and Al_2O_3 are preferred from among these.

To produce the outer shell in the shell-type catalyst materials with an average agglomerate size range up to 15 µm, preferably with an agglomerate size in the range from 2 to 10 µm are employed. The use of finely divided silica with an agglomerate size range of 3 to 7 µm is particularly preferred.

Larger agglomerates/particles are generally not particularly advantageous for the preparation, since they cannot form homogeneous, firmly adhering, abrasion-resistant shells, as a result of their size.

The metal oxides used herein have a surface area in the range from 50 to 500 m^2/g, preferably 100 to 300 m^2/g and a compacted density (according to DIN/ISO 787/11XI, JISK 5101/18) in the range from 10 to 800 g/l, preferably 50 to 500 g/l.

Silicas which have the surface areas and compacted densities mentioned above are particularly appropriate.

The shell-type catalysts prepared using the metal oxides mentioned are largely homogeneous, as demonstrated by their scanning electron microscope photographs, exhibit no troughs apart from macro indentations (in which the coated materials may accumulate), and also do not produce cracks at the surface of the support. At very high magnifications, a largely homogeneous granular structure can be detected.

The thickness of the outer shell on shell-type catalysts prepared according to the invention may be very accurately controlled over a wide range. It is preferably in the range from 0.1 to 20 µm. Ranges from 0.5 to 10 µm are particularly preferred. It is extremely expedient that the shell has a thickness of greater than 1 µm.

The ratio of noble metal compound soluble in water to coating compound substantially insoluble in water, in the suspension to be dried onto the support material, can be varied over a wide range. A preferred process according to the invention is characterised in that the noble metal compound which is soluble in water and the coating compound which is substantially insoluble in water, each with respect to the metal content, are used in a ratio by weight of noble metal compound to coating compound within the range 0.1 : 1 to 5 : 1. A variant in which the noble metal compound and the coating compound are used in a ratio by weight within the range 0.5 : 1 to 2 : 1 is particularly expedient.

Furthermore it is expedient that the noble metal compound, with respect to the total weight of shell-type catalyst, is used in a ratio by weight, calculated as metal, in the range 0.0001 : 1 to 0.02 : 1.

In addition, it is of particular importance that the coating compound, with respect to the total weight of shell-type catalyst and calculated as metal, is used in a ratio by weight in the preferred range of 0.0005 : 1 to 0.005 : 1.

The concentration of metal, in particular palladium or platinum, in the shell-type catalyst, as it is prepared by the process according to the invention, is preferably at most 1 wt.% metal, in particular in the range between 0.1 and 0.5 wt.% metal. Metal contents, in particular palladium contents, of less than 0.1 wt.% are not meaningful, since the catalyst can lose noble metal as a result of abrasion in a real situation and under real process conditions so that low noble metal contents would produce too short a service lifetime. Noble metal contents greater than 1 wt.% are also not particularly useful, since these can lead to unwanted thickening of the layer of noble metal, associated with a reduction in adhesion as a result of the very low surface area of the support material, and an increased performance potential cannot be achieved in this way. The concentration of coating materials in the shell preparations according to the invention is preferably in the range from 0.05 to 1 wt.%, expressed as metal. The concentration is particularly preferably 0.05 to 0.5 wt.%, expressed as metal, with respect to the total weight of catalyst. When adding this order of magnitude of the preferred finely divided coating material, a surprisingly good adhesive effect is obtained.

In accordance with the second step of the process according to the invention, the shell formulations are converted to activated shell-type catalysts in a reducing gas stream. This treatment consists of the selective reaction of one of the alloy components with a gas or a gas mixture at elevated temperature.

It is particularly preferred that a gas stream containing hydrogen is used for activation.

To improve the adhesion between support and material to be dried it is possible to add adhesion promoters which are familiar to a person skilled in the art per se, e.g. waterglass. These are added to the suspension and applied to the support in the same process step.

In the same way, it is also possible to add additional doping compounds to the suspension in order to facilitate specific effects relating to the activity/selectivity of the catalyst.

The invention also provides use of the shell-type catalysts obtainable by the procedure described herein for the selective hydrogenation of acetylene in gas streams. The shell-type catalysts which can be prepared according to the invention are particularly advantageously used in gas streams for the purification of hydrogen chloride gas in the vinyl chloride process.

Thus a shell-type catalyst is preferably obtained within the scope of the invention which is prepared by drying-on a suspension consisting of a noble metal salt solution, preferably a palladium salt solution, with a finely divided material, preferably silica, and then reducing with a reducing, preferably hydrogen-containing gas, which is based on support materials with low surface areas and which is characterised by high activity and selectivity at high space velocities of up to 8000/h, in the range 2000 - 6000/h, for the purification of a hydrogen chloride gas stream by selective hydrogenation of the acetylene contained therein to give ethylene.

The process conditions which are particularly suitable for this are as follows:

Temperature range 100 - 200°C, preferably 100 - 160°C;

Pressure range for hydrogen chloride gas stream (process pressure) 1 to 15 bar absolute, preferably 6 - 12 bar, depending on the process pressure for oxychlorination;

Residence time 2 - 15 sec (under the operating conditions and with an empty tube);

Hydrogen to acetylene ratio 1 : 1 to 6 : 1, preferably 2 : 1 to 4 : 1;

In the following, the invention is explained in more detail using examples and making reference to the enclosed Figures 1 to 3.

Having thus generally described the invention, reference will now be made to the drawings, illustrating preferred embodiments and in which:

Fig. 1 is a graphical representation of conversion/ selectivity/abrasion characteristics of the shell-type catalyst according to the invention as a function of the proportion of coating material;

Fig. 2 is a histogram illustrating conversion/selectivity of catalyst according to comparison example 1 as a function of space velocity; and

Fig. 3 is a histogram illustrating conversion/selectivity of the catalyst in accordance with the invention, according to example 2 (shell-type catalyst) as a function of space velocity.

Fig. 1 shows the variation of performance potential (conversion/selectivity) and abrasion of a shell-type catalyst in accordance with the invention, prepared with a palladium salt solution on an SiO_2 granulate with granularity 3 - 5 mm, with concentration of silica with an average agglomerate size of 7 µm. The conversion and selectivity data were determined in a laboratory test apparatus at 130°C. The test gas used had the following composition:

0.5 % hydrogen / 0.2 % acetylene / 99.3 % nitrogen.

Figure 1 shows clearly that, at concentrations of greater than 0.25 wt.% of silica, a clear increase in abrasion occurs without producing a substantial increase in conversion or selectivity. From silica concentrations of 0.1 wt.%, substantial increases in conversion and increased space velocity as compared with a catalyst preparation without added silica are indicated. Thus the particularly preferred proportion of silica, with respect to the total weight of catalyst, in the catalyst mentioned by way of example is 0.1 - 0.3 wt.% of the preferably used silica.

A shell-type catalyst with the composition described of 0.1 - 1 wt.% Pd and 0.1 - 1 wt.% silica on a nonporous SiO_2 support with granularity 3 - 5 mm and a low surface area of less than 1 m^2/g is characterised by a very high activity and selectivity at space velocities of up to 8000/h, preferably 2000 - 6000/h, during the selective hydrogenation of acetylene in a hydrogen chloride gas stream under the process conditions described above, which is used by way of example.

The increased activity of the catalyst according to the invention is a result of improved fine distribution of the noble metal integrated into the preferably applied silica shell. The silica brings about this fine distribution effect by promoting an enlargement of the surface area. In comparison, in the case of porous impregnated support materials, the additional reactive centres at the surface of the support provide an additional potential for unwanted secondary reactions.

The shell-type catalyst in the present invention has an extended activity potential. For the application mentioned by way of example, high acetylene conversions are achieved in a GHSV range of up to 8000/h during hydrogen chloride gas purification. The selectivity to give ethylene is more than 60%.

When preparing the shell-type catalysts in the present invention, drying of the suspension of noble metal salt, preferably a palladium salt, and finely divided coating material, preferably silica, with the ultimate production of a homogeneous shell is performed in a moving bed; i.e. the suspension of noble metal salt and preferred silica is thoroughly mixed with the support and the solvent water is removed by distillation with external heating.

As a result of the method of preparation and the production of a surface shell, the addition of various doping and adhesion promoting substances is also very easy and is associated with corresponding effects on shell modification and performance characteristics. Preferred doping additives are known from the literature (e.g. D.L. Trimm, Design of Industrial Catalysts, Elsevier Scientific Publ. Comp., 1980, pp. 229 *et seq*).

Comparison Example 1:

- Standard catalyst without added silica -

The catalyst was prepared in a moving bed. An SiO_2 granular material which was washed with caustic and then washed acid-free was initially placed in the preparation drum. The corresponding amount (0.15 wt.% Pd with respect to weight of catalyst) of palladium chloride solution was added to the drum with the continuous passage of a stream of nitrogen. The palladium salt solution was dried onto the support in the rotating drum by passing pressurized steam (140°C) through the external jacket of the preparation drum. Reduction was achieved by passage of an excess amount of hydrogen gas through the periodically rotating preparation drum. The stream of hydrogen gas was finally replaced by a stream of nitrogen gas in the subsequent cooling phase.

The catalyst obtained by this method of preparation has a grey/glossy but thin external noble metal shell of less than 1 μm.

Example 2:

- Preparing a shell-type catalyst -

Different from preparing the standard catalyst in example 1, preparation of the shell-type catalyst was started by introducing 0.5 t of dry SiO_2 granules. Then the amount of dry silica corresponding to 0.25 wt.% of the catalyst was introduced to the preparation drum. An amount of palladium nitrate solution corresponding to 0.15 wt.% of the catalyst was then added to the preparation drum. After a period of action under nitrogen in a rotating drum, drying was performed at 140°C in the same way as in example 1. Reduction was achieved by introducing forming gas (5% hydrogen in nitrogen) into the bed of dried catalyst.

The catalyst obtained was a deep black colour and had a matte finish. Table 1 gives a comparison of the physical properties of the catalysts described in preparation examples 1 and 2.

Table 1:

Parameters:	**Catalyst according to comparison example 1** **-standard catalyst-**	**Catalyst according to example 2** **-shell-type catalyst-**
Pd conc. [wt.%]	0.15	0.15
Proportion of silica [wt.%]	0	0.25
Appearance	grey/glossy	matte/black
Abrasion [wt.%] ASTM D 4058-87	0.2 - 0.3	0.4 - 0.5
BET surface area [m^2/g]	no adsorption	< 1
CO-adsorption [10^{-2} ml/g]	0.3	1.25

Performance Comparison:

Application example I

Comparison tests 1 and 2

The catalysts described under comparison example 1 and example 2 were tested with regard to their conversion and selectivity potential in a pilot plant.

The pilot plant was incorporated as a bypass reactor unit in an existing hydrogenation unit for purification of the hydrogen chloride gas stream within a vinyl chloride production plant, so that an actual hydrogen chloride gas stream containing up to 2000 ppm of acetylene could be passed directly over the catalyst. Two reactors were installed in parallel so that, in one reactor, a reference catalyst could be tested while new developments were being introduced in the reactor connected in parallel. Thus, a direct comparison was possible under varying plant conditions and with varying quality of the hydrogen chloride. The reactors were designed so that they can be filled with 2 l of catalyst. They were heated by heating coils containing pressurized steam. Hydrogen can be added in flexible amounts via a rotameter and each reactor has a temperature measuring device (in the middle of the catalyst bed) which could be used for temperature regulation.

The maximum volume of hydrogen chloride which can be passed through each reactor is 16 Nm^3/h. After emerging from the reactors, the reaction gas was supplied separately to a gas chromatography unit for analysis.

Performance Comparison

The catalysts described in comparison example 1 and example 2 were tested for several months in the pilot plant under varying conditions. The requirement for primary performance comparison was, *inter alia*, to fix the rate of conversion and then to determine the corresponding space velocity as a direct measure of performance. The comparable settings are given in tables 2 and 3.

Table 2:

Settings I:

Quantity compared	Catalyst according to comparison example 1 -standard catalyst- Reactor A	Catalyst according to example 2 -shell-type catalyst- Reactor B
Running time [weeks]	8	8
Temperature	130	130
$H_2 : C_2H_2$ ratio	2	2
Conversion of C_2H_2 [%]	90	91
Selectivity to give C_2H_4 [%]	51	63
GHSV [1/h]	750	4500

Table 3:

Settings II:

Quantity compared	Catalyst according to comparison example 1 -standard catalyst- Reactor A	Catalyst according to example 2 -shell-type catalyst- Reactor B
Running time [weeks]	12	12
Temperature	130	135
$H_2 : C_2H_2$ - molar ratio	2	2
Conversion of C_2H_2 [%]	70	73
Selectivity to give C_2H_4 [%]	52	61
GHSV [1/h]	1500	6000

The performance comparison given in tables 2 and 3 for fixed conversion shows clearly the increased performance potential of the shell-type catalyst in accordance with this invention in the particular application of hydrogen chloride gas purification. The shell-type catalyst can be used at 4 - 6 times higher space velocities to produce the same ethylene selectivity.

Conversion/Selectivity Characteristics

The conversion and selectivity characteristics of the catalysts described in examples 1 and 2 were determined at different space velocities and are summarized in table 4.

Table 4:

Basic settings:

Temperature (middle of bed): 130°C; H_2 : C_2H_2

Molar ratio = 2

Catalyst according to comparison example 1 -standard catalyst- Reactor A			**Catalyst according to Example 2 -shell-type catalyst- Reactor B**		
GHSV	Conversion of C_2H_2 [%]	Selectivity to give C_2H_4 [%]	GHSV	Conversion of C_2H_2 [%]	Selectivity to give C_2H_4 [%]
750	90	52			
1000	82	57			
1500	70	52			
2250	60	64	2250	100	39
			4500	91	63
6000	16	60	6000	73	61

Graphical Representation in Figs. 2 and 3

The conversion/selectivity characteristics of the shell-type catalyst according to the invention demonstrate that, as compared with a standard catalyst (according to the prior art), much higher space velocities can be used without incurring a decrease in conversion. In the high GHSV range from 4000/h upwards very advantageous, preferred conversion and selectivity combinations are produced.

Although embodiments of the invention have been described above, it is not limited thereto and it will be apparent to those skilled in the art that numerous modifications form part of the present invention insofar as they do not depart from the spirit, nature and scope of the claimed and described invention.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for preparing a shell-type catalyst in which a nonporous inorganic support material having a BET surface area of less than 80 m^2/g is provided with a catalytically active outer shell, comprising:
providing a suspension of at least one noble metal compound which is soluble in water;
providing a coating compound substantially insoluble in water;
drying said suspension and said coating compound onto said support material;
coating a dried and coated support material with an outer shell; and
activating said support coated with said outer shell with a reducing gas.

2. The process according to claim 1, wherein said support material comprises at least one of moulded articles made of glass, quartz, ceramic, silicon dioxide, aluminium oxide, graphite, moulded carbon, metal or steatite.

3. The process according to claim 2, wherein said support material includes at least one of SiO_2 or Al_2O_3.

4. The process according to one or more of the preceding claims, wherein said support material is in a form of at least one of hollow extrudates, solid extrudates, spheres, granules, tablets or strands.

5. The process according to one or more of the preceding claims, wherein said support material has particle diameters in the range from 0.5 to 50 mm.

6. The process according to one or more of the preceding claims, wherein said support material has a BET surface area of less than 10 m^2/g.

7. The process according to any one of the preceding claims, wherein said support material has a pore volume of less than 0.5 ml/g.

8. The process according to claim 7, wherein said support material has a pore volume of less than 0.1 ml/g.

9. The process according to any one of the preceding claims, wherein said support material has an Fe_2O_3 content of less than 0.5 wt.%.

10. The process according to any one of the preceding claims, wherein said noble metal compounds comprise at least one of Ru, Rh, Pd, Ag, Os, Ir, Pt or Au.

11. The process according to claim 10, wherein at least one of oxides, hydroxides, carbonates, halides, nitrates, salts of organic acid or complex compounds of said noble metal compounds is employed in said process.

12. The process according to any one of the preceding claims, wherein said noble metal compound is an aqueous solution containing said noble metal compound at a concentration of greater than 1 wt.% metal.

13. The process according to claim 12, wherein said noble metal compound is an aqueous solution containing said noble metal compound at a concentration of greater than 5 wt.% metal.

14. The process according to any one of the preceding claims, wherein said noble metal compound is soluble in water at 30°C at a concentration, calculated as metal, of at least 0.01 wt.%.

15. The process according to any one of the preceding claims, wherein said coating compounds are selected from metals soluble in water at 30°C at a concentration, calculated as metal, of less than 4 wt.%.

16. The process according to claim 15, wherein said compounds includes at least one of SiO_2, Al_2O_3, TiO_2 or ZrO_2.

17. The process according to claim 16, wherein said compound has an average agglomerate size of 15 µm.

18. The process according to claim 17, wherein said agglomerate size is between 3 - 7 µm.

19. The process according to any one of claims 15 to 18, wherein said compound has a BET surface area in the range of 50 - 500 m^2/g.

20. The process according to any one of claims 15 to 19, wherein said compound has a compacted density in the range of 10 - 800 g/l.

21. The process according to any one of the previously mentioned claims, wherein said noble metal compound which is soluble in water and said coating compound which is substantially insoluble in water, each with respect to metal content, are used in the ratio by weight of noble metal compound to coating compound in the range from 0.1 : 1 to 5 : 1.

22. The process according to claim 21, wherein said noble metal compound to coating compound are used in a ratio by weight in the range 0.5 : 1 to 2 : 1.

23. The process according to any one of the previously mentioned claims, wherein said noble metal compound, based on total weight of shell-type catalyst, is used in a ratio by weight, calculated as metal, in the range from 0.0001 : 1 to 0.02 : 1.

24. The process according to any one of the previously mentioned claims, wherein said coating compound, based on total weight of shell-type catalyst and calculated as metal, is used in the ratio by weight in the range from 0.0005 : 1 to 0.04 : 1.

25. The process according to claim 1, wherein said gas stream contains hydrogen.

26. The process according to any one of the previously mentioned claims, wherein said adhesion promoters are added to said suspension to be dried onto the support.

27. The process according to any one of the previously mentioned claims, wherein said additional doping compounds are added to said suspension.

28. Use of a shell-type catalyst obtained according to the previously mentioned claims for the selective hydrogenation of acetylene in gas streams, in particular hydrogen chloride gas in the vinyl chloride process.

Fig. 1:

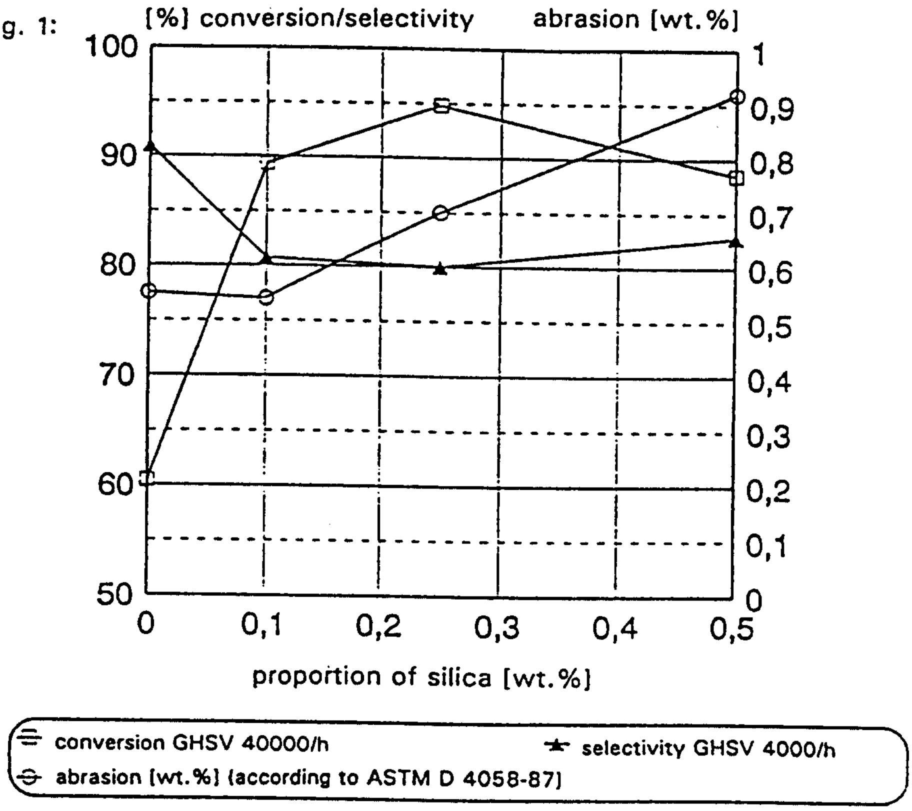

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Fig. 2:

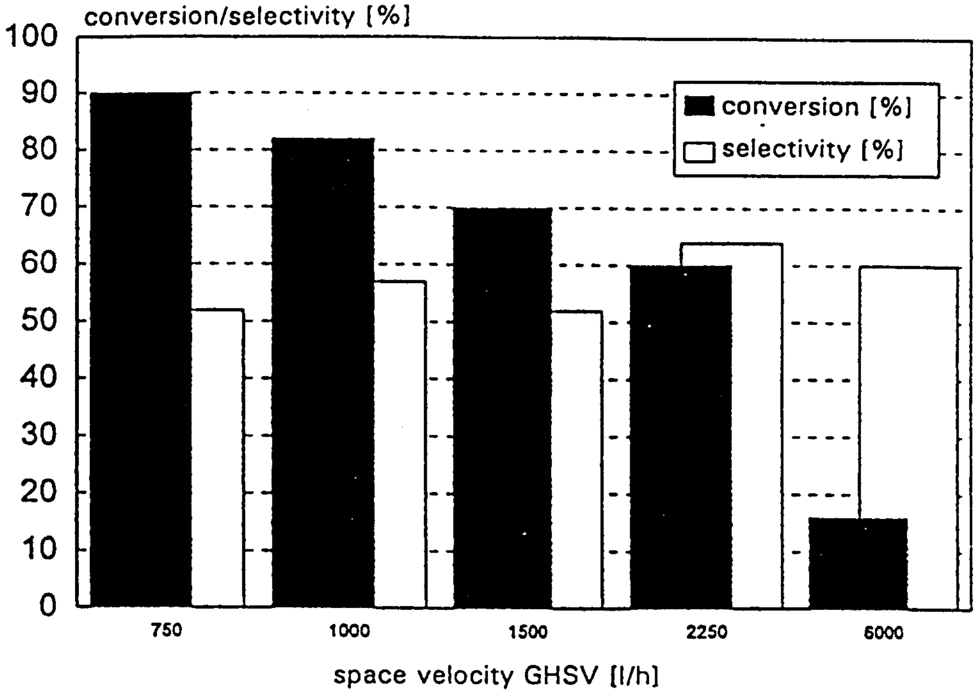
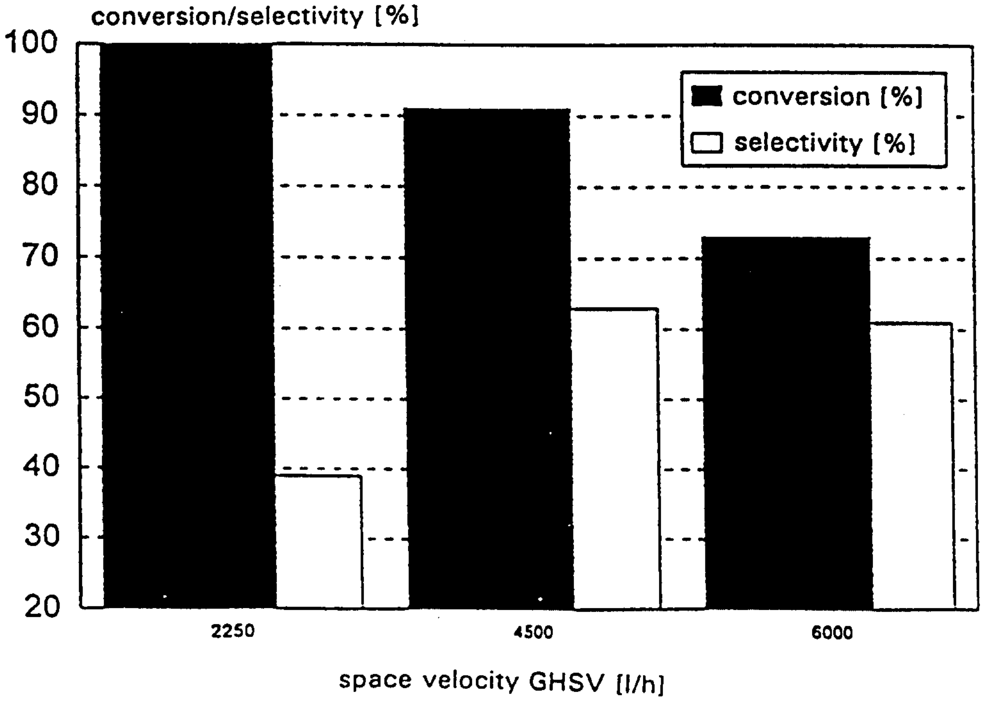


Fig. 3:



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