

Title: Ceramic coating

The invention relates to thin ceramic layers applied to non-porous or : coarse-porous ceramic or metallic substrates. 'Coarse-porous' in this connection is understood to mean containing pores of a diameter of about 1 mm or more. The invention comprises both non-porous and hence non-permeable ceramic layers and
5 (high-)porous ceramic layers. 'Thin' is understood to mean a thickness of less than 1 mm to a thickness of about 100 mm.

Non-porous ceramic layers are applied as glazing to ceramic substrates and as enamel to metallic substrates. The aim of applying the layers is generally protection or embellishment. The invention is directed especially to the use of thin
10 ceramic layers in the protection of metals and alloys. Primarily, this involves screening against the attack of the metal or the alloy by reaction with carbon-containing gas molecules. It has been observed that upon exposure of metal and alloy surfaces to carbon-containing gas molecules, such as methane or higher hydrocarbons or a mixture of carbon monoxide and hydrogen, metal or alloy
15 particles disappear from the surface. As a result, the thickness of the metal or the alloy can decrease rapidly, giving rise to fracture in equipment working under increased pressure. In cases where work is not done under pressure, the loss of metal or the alloy causes leakage. In other cases, the exposure of metals or alloys to hydrocarbons at increased temperature leads to the deposition of a relatively
20 dense layer of carbon on the metal or alloy surface. The layer of carbon appears to strongly decrease the heat transfer from the metal or alloy wall to a gas stream. In many technically important cases, such as, for instance, in naphtha cracking plants, a significant reduction of the heat transfer is unallowable, since the capacity of the plant decreases strongly as a result. The plant must then be
25 stopped and the carbon layer must be removed by oxidation. In general, this occurs by reaction with oxygen or with steam. Technically, it is of great importance to protect metal or alloy surfaces against loss of metal or alloy particles or against the deposition of carbon layers by the use of a suitable coat. According to the present state of the art, the application of such a protective layer
30 has been found not to be properly possible. It has been attempted, by starting from an aluminum-containing alloy, to apply a protective aluminum oxide layer to the

metal surface. An example of such an alloy is Fecralloy. In practice, however, a layer formed in such a way was found not to protect the metal surface sufficiently. An additional drawback of Fecralloy is that this alloy, like other aluminum-containing alloys, cannot be welded.

5 In general, the fact that aluminum-containing alloys cannot be welded is a drawback of alloys that are resistant to oxidizing gases at highly increased temperature. A second object of the present invention is therefore to provide non-permeable, oxidation-resistant ceramic layers on metals of good weldability. In that case, the metals or alloys can first be brought into the desired form by
10 welding, whereafter the protective layer is applied.

 In this connection, the invention is directed especially to rendering metal gauzes resistant. In catalytic reactions at (strongly) increased temperature, because of the intrinsic high reaction rate, no large catalytically active surface area per unit of volume is necessary. The surface area of a metal gauze is then
15 sufficient. Further, the pressure drop upon passage of a gas stream through one or more metal gauzes is very low. In the oxidation of ammonia to nitrogen oxide in the production of nitric acid, use is therefore made of platinum or palladium gauzes, to which often small amounts of other precious metals have been added. A major drawback is that the precious metal disintegrates during the catalytic
20 reaction. Initially, use was made of a gauze of gold, arranged under the platinum gauze to catch the platinum particles. Later, a platinum gauze was used to catch the small platinum particles formed. In that case, no platinum-gold separation is needed to recover the platinum. If, in fact, no catalytic reaction proceeds over the precious metal, such as platinum or palladium, the precious metal does not
25 disintegrate. To increase the productivity of nitric acid factories, it is highly attractive to work with pure oxygen instead of air; also at increased oxygen pressure the productivity increases strongly. However, because of the greatly accelerated disintegration of the precious metal gauze at higher oxygen pressure, this has not been found possible so far. Applying the precious metal in finely
30 divided form to a stabilized gauze would enable an important improvement of the nitric acid process. This process has not been fundamentally improved since the invention by Ostwald at the end of the nineteenth century.

In the Andrussov process, in which, at temperatures above about 1000°C, ammonia is reacted with methane to hydrogen and hydrogen cyanide, also a precious-metal gauze is used. In this case too, a stabler metal gauze is of great significance. Finally, processes are currently being worked on, to produce
5 synthesis gas, a mixture of carbon monoxide and hydrogen, by contacting a stream of methane and pure oxygen with a catalyst, for instance platinum, at temperatures above 1000°C. Such processes too could highly advantageously utilize precious metals applied in finely divided form to stabilized metal gauze.

Obviously, within the framework of enameling, much research has
10 already been done on the application of protective ceramic coatings to metal and alloy surfaces. Thus the conditions and the chemical composition necessary to accomplish a good bonding to the metal are generally known. However, it has been found to be very cumbersome to apply an enamel having a softening point or melting point that lies at a high temperature with a homogeneous chemical
15 composition as a thin uniform layer to metal or alloy surfaces. A thin layer is necessary, since a thick layer, due to the difference in coefficient of expansion, readily chips off the substrate upon heating or cooling. Also, according to the present state of the art, it is cumbersome to accurately set the chemical composition of the protective ceramic layer. This is also an important objective of
20 the present invention.

In the use of porous ceramic layers on solid surfaces, an object can be to provide protection against attack of the metal or the alloy upon exposure to a high-temperature gas stream. Considered in particular in this connection are gas turbines, where the metal or the alloy exhibits too low a mechanical strength at
25 the desired high temperatures. In that case, use can be made of a porous layer of a thermostable material which, through an effectively low heat conductivity of the porous layer, leads to a temperature profile over the porous layer such that the temperature of the metal or the alloy does not exceed a particular limit value. Firm anchorage of such a porous layer, when used in gas turbines, is obviously an
30 important condition.

A second use contemplated with the invention is the use of a porous layer applied to a solid surface as catalyst. According to the prior art, such layers are applied to solid surfaces by using so-called dip coating techniques. In this

connection, there are two different ways of proceeding. These two procedures relate to the fact that most catalytically active materials sinter strongly under conditions of the required thermal pretreatment or of the catalytic reaction.

To prevent sintering of the catalytically active material and the consequent loss of surface area and hence of activity, in general the catalytically active material is applied to a high-porous thermostable material, a so-called support. The most commonly used catalyst support materials are aluminum oxide and silicon oxide. According to the first procedure, a finely divided support material is loaded with the catalytically active material or a precursor thereof. This thus loaded support material is then applied to the solid surface. According to the second procedure, the unloaded support is deposited on the surface, whereupon the catalytically active component or a precursor thereof is provided in the porous support layer.

In both cases, the surface to be covered is immersed in a suspension of the catalytically active material or of the support, and the surface is removed from the suspension at an empirically determined rate. This method is known by the name of dip-coating or wash-coating. Depending on the viscosity and the other properties of the suspension, a layer of the catalytically active material of a particular thickness then deposits on the substrate. For the production of exhaust gas catalysts, this method is presently used on a large scale. Used as substrates are, virtually exclusively, ceramic monoliths. To date, however, no successful attempts have been made to modify the dipcoat or washcoat process such that firmly anchored catalytically active layers can be applied to metal surfaces.

According to the prior art, a high-porous layer exhibiting better bonding can be applied to ceramic and metallic surfaces by starting from solutions of silicone rubber or titanium and zirconium compounds as the ammonium salt of a chelate with lactic acid of a titanate or a chelate of diethyl citrate of a zirconate. See EP-B 571508. By dipping or by spin-coating, a thin layer of such an elastomer can be applied to the surface to be covered. Pyrolysis of the thin layer of the elastomer resulting after drying then leads to a high-porous layer of a ceramic material. A so prepared layer of silicon dioxide maintains the porosity up to temperatures of about 700°C. The thermal stability of the ceramic layer, as well as the pore distribution of the layer, can be set by adding, for instance, aluminum compounds to the solution of silicone rubber. A compound suitable for this purpose

is, for instance, aluminum sec-butoxide. Mixtures of silicone rubber and titanium and zirconium compounds as the ammonium salt of a chelate with lactic acid of a titanate or a chelate of diethyl citrate of a zirconate can be used to apply silicon dioxide with an adjustable amount of titanium dioxide or zirconium oxide.

5 In general, the thus obtained ceramic layers contain no catalytically active components. According to the present state of the art, those are provided by impregnation of the porous ceramic layer with a solution of a precursor of the catalytically active material. Through a thermal treatment, the precursor can be converted to the desired catalytically active component.

10 The present state of the art also encompasses wholly or partly converting a porous silicon dioxide layer applied to a solid substrate to a synthetic clay mineral. See also WO-A-9607613.

Clay minerals are catalytically of interest as solid acid catalysts.

The application of catalytically active materials to solid, non-porous or
15 little porous surfaces has been found to be of great value when used in gas streams where a low pressure drop is essential. As mentioned above, in many such cases monoliths are used. Also other materials with a low pressure drop have been developed, whereby an intensive contact between a gas stream and a catalyst surface is effected. Examples are sintered metals, ceramic and metallic foams and
20 in particular special reactor packings of specially shaped metal foils. The action of special reactor packings has been described by G. Gaiser and V. Kottke in Chem.-Ing.-Technik 61 (1989) no. 9, pp. 729-731. With all these materials, it is a requirement that the catalytically active material can be applied to the surface of the structure of the reactor packing so as to be firmly anchored thereon.

25 Another motive to apply the catalytically active material to a solid surface is the supply and removal of reaction heat in endothermic and exothermic reactions, respectively. When use is made of a fixed catalyst bed, it is generally cumbersome to supply or remove the heat of reaction. If in an exothermic or endothermic reaction the temperature is to be properly controlled, as in the
30 oxidation of ethylene to ethylene oxide, and it has still been decided to use a fixed catalyst bed, the catalyst is to be applied in a great many (e.g. 20,000) relatively thin tubes. This renders the reactor costly, while the filling of such a large number

of tubes with catalyst to the same pressure drop is very time-consuming and labor-intensive.

Now, it has been proposed to use reactors in which metal bodies, such as for instance spheres of a diameter of 1 mm to 1 cm or more, are sintered together and sintered to the reactor wall. This yields a high thermal conductivity. In this case, it is necessary to apply the catalyst as a porous layer of a thickness up to, for instance, 1 mm on the surface of the sintered metal bodies.

A last area where catalytically active materials applied to solid surfaces can be of great significance is that of catalytic liquid-phase reactions or that of catalytic reactions where a gaseous with a liquid reactant occur, as in catalytic hydrogenation or oxidation reactions. According to the present state of the art, in these reactions, work is done with suspended catalysts or with a fixed catalyst bed through which the reactants are passed. Well known is the use of a fixed catalyst bed through which a liquid reactant together with a gas stream is allowed to flow down, a so-called trickle flow process. In a fixed catalyst bed, catalyst bodies with dimensions of at least a few millimeters must be used, because otherwise the pressure drop becomes too high. Because of the low diffusion coefficient in liquids, consequently, in a fixed catalyst bed only the outer edge of the catalyst bodies contributes effectively to the catalytic reaction. Not only does this involve poor utilization of the catalyst, but it may also have a highly adverse effect on the selectivity of the catalytic reaction. In suspended catalyst bodies, much smaller catalyst bodies can be used, for instance of dimensions of 3 to 100 μ m. Now the utilization of the catalyst is much better and the selectivity is not impaired. When using such small catalyst bodies, however, the separation of the catalyst from the reactor product through settlement and decanting, filtration or centrifugation is laborious. Also, the catalyst bodies are often subject to wear, so that extremely small catalyst particles cannot be separated from the product and the reaction product is contaminated.

When applying the catalyst as a thin layer on a solid surface, the advantages of the fixed catalyst bed, no separate separation of the catalyst, are combined with those of a suspended catalyst, efficient utilization of the catalyst and good selectivity. Also, a suitable flow pattern of the liquid, and possibly the

gas, around the catalyst can be realized. Thus it is possible first to mix the reactants very intimately before they come into contact with the catalyst.

Surprisingly, it has been found that a properly protective coverage of a metal, an alloy or a ceramic material can be obtained with a non-porous,
5 non-permeable ceramic layer of a thickness of less than 100 mm, preferably of a thickness of less than 5 mm, and still more preferably of a thickness of less than 1 mm, which has been bonded onto the surface through an intermediary layer which contains ions of the surface to be covered, while in the case of substrates consisting of metals or alloys the oxide of the covered material is not demonstrable
10 with X-ray diffraction. Figure 1 gives a schematic representation of such a layer and the substrate. Surprisingly, it has been found that a thin porous ceramic layer applied to a ceramic or metallic substrate, upon treatment at a sufficiently high temperature, can be converted to a dense, non-permeable layer. According to the known state of the art, a thin porous layer is applied by pyrolysis of a thin layer of
15 a suitable elastomer, such as silicone rubber, applied to the surface to be protected. For applying thicker layers, according to the known prior art, use will be made of dip-coating or spin-coating a suspension of the material to be applied. The thickness of the layer can be varied within wide limits, for instance from less than 1 to more than 100 mm. If necessary, if relatively thick layers are desired,
20 several layers are applied one after another. It has been found to be advantageous to pyrolyze each elastomer layer after the application thereof, before a new layer is applied. With thin layers, the difference in thermal expansion of the ceramic layer and the substrate plays a comparatively minor role. The application of layers of a thickness of less than 5 mm and preferably less than 1 mm is therefore of
25 great advantage. It has been found that thin layers can be obtained best starting from thin layers of pyrolyzed silicone rubber. Because of the good bonding of silicone rubber to substrates, it is relatively easy to apply a thin layer of a uniform thickness to substrates of greatly divergent materials. Pyrolysis of such layers leads to a thin layer of porous silicon dioxide of uniform thickness. Upon sintering,
30 preferably in an inert gas atmosphere, this readily yields a non-porous, non-permeable layer of a uniform thickness which fully covers the substrate.

Most easily, according to the invention, thin protective ceramic layers can be obtained by applying a thin layer of silicone rubber and pyrolyzing this

material first at a temperature of about 450°C and thereupon sintering the layer in an inert gas atmosphere at a greatly increased temperature to a non-porous, non-permeable layer. According to a special embodiment of the invention, the thin protective non-permeable layer therefore consists substantially of silicon dioxide.

5 To effect good bonding of the ceramic layer to metal or alloy surfaces, the metal surface needs to be covered with a thin oxide layer. When this layer is too thick, no good bonding is obtained. In traditional enameling this is a problem: For use at high temperatures, a ceramic layer having a high softening or melting temperature must be applied. When the softening temperature or the melting
10 point of the enamel is high, the metal or alloy surface, upon application of the layer, is oxidized too strongly. The result is then a less good bonding. Surprisingly, it has now been found that the pyrolysis of the layer of the elastomer obtained after drying leads to an exceedingly firmly anchored porous layer. On a metal like aluminum, too, provided that the surface is sufficiently degreased and cleaned, an
15 excellent bonding is obtained. The conversion at higher temperature, following the pyrolysis, to form a non-porous, non-permeable layer, is therefore preferably carried out, in accordance with the invention, in an inert gas atmosphere. The fact is, it has been found that transport of oxygen through the initially porous ceramic layer at increased temperatures can lead to strong oxidation of the metal at the
20 interface with the ceramic layer. The metal oxide formed then presses the ceramic layer off the metal or alloy surface. In the pyrolysis of the dried layer of the elastomer, sufficient metal oxide is formed to effect a very good bonding. A great advantage of thin layers according to the invention is that these layers can be very thin, while the metal surface is still completely or virtually completely covered.
25 A properly sealing layer of a thickness of less than 1 mm can be readily obtained.

The chemical composition of the ceramic layer can be adjusted as desired. First of all, this is possible by setting the composition of the solution of the elastomer by adding, in accordance with the state of the art, to, for instance, silicon dioxide, certain components, such as aluminum oxide or titanium dioxide.

30 It is of importance to be able to manage the chemical composition of the layer substantially consisting of silicon dioxide so as to control the melting point of the layer and hence the temperature needed to come to a non-permeable, non-porous layer. When it is desired to use the protective ceramic layer at highly elevated

temperatures, it is of importance to set the softening point of the ceramic layer as high as possible. This can be done by incorporating aluminum oxide or titanium dioxide into the silicon dioxide. Thus, to a solution of silicone rubber in ethyl acetate or in diethyl ether, an alcoholate of aluminum can be added, such as the isopropoxide. Titanium and zirconium compounds can be added as the ammonium salt of a chelate with lactic acid or a titanate or a chelate of diethyl citrate of a zirconate. For pure silicon dioxide, such as it is obtained by pyrolysis of silicone rubber, a temperature above about 800°C is needed to obtain a non-porous layer. When it is intended to work with the protective layer at a lower temperature, it is attractive to obtain a dense, non-permeable layer by sintering at a lower temperature. According to a special embodiment of the method according to the invention, the method therefore starts from a water glass solution when the covered metal or alloy surface is not subsequently exposed to very high temperatures. Surprisingly, it has been found that with a water glass solution, a thin, non-porous, strongly bonding layer can be readily applied to metal and alloy surfaces. It is also possible first to apply a porous layer of silicon dioxide from silicone rubber, and then to impregnate water glass into this layer and finally to carry out a treatment at increased temperature to come to a properly sealing, non-porous layer.

The addition of titanium compounds readily leads to acid-resistant enamel layers, which are part of the invention. According to the method of the invention, such layers can be readily applied to the wall of reactors. Alkali-resistant layers are obtained according to the invention by adding zirconium to silicon dioxide, alone or in combination with tin oxide. According to the invention, boron oxide is added preferably by addition of suitable boron compounds, such as for instance aluminum borohydride, to the solution of the elastomer.

A second procedure for incorporating certain components into the initial porous layer is impregnation of the porous layer with solutions of suitable compounds or deposition-precipitation of certain compounds in the porous layer. These procedures are attractive especially for the application of components such as nickel oxide and cobalt oxide. Reaction with the silicon dioxide can be readily obtained by deposition-precipitation of these elements, but impregnation is also attractive in many cases. It is known that nickel oxide and cobalt oxide greatly

improve the bonding of silicon dioxide-containing layers to metal and alloy surfaces. According to the invention, the impregnation of a suitable solution of components to be included in the ceramic layer is preferably done in the evacuated layer, whereby a volume of solution is impregnated which corresponds to the pore
5 volume of the porous layer.

For catalytic applications at temperatures above about 700°C, the magnitude of the exposed catalytically active surface is generally of less importance than the (thermal) stability of the catalyst system. Therefore, according to the invention, a metal or ceramic covered with a non-porous,
10 non-permeable ceramic layer is used as catalyst support. The catalytically active material is applied to this surface in, if necessary, finely divided form. In this embodiment, the invention is preferably practiced with gauze-shaped metal substrates. Figure 2 schematically represents such a surface.

When the catalytic reaction is operated at lower temperatures, the
15 reaction on the catalytically active surface typically proceeds at such a rate that the transport of the reacting molecules in the pores of the catalyst occurs sufficiently fast. In that case, a large catalytically active surface area per unit of volume of the reactor is of great significance. According to a special embodiment of the invention, therefore, on a ceramic or metallic surface, first a protective
20 non-porous, non-permeable layer is applied, whereafter a porous ceramic layer is deposited on the non-porous layer. In the porous layer, active components can be provided in finely divided form. The distribution over the surface of the porous material leads to a thermostable catalyst. Firstly, the non-porous, non-permeable layer causes the metal to be oxidized upon the thermal pretreatment necessary to
25 provide a next porous layer or to activate a precursor of a catalytically active component. Oxidation of the metal surface leads to a greatly reduced bonding of the porous layer to the metal. Figure 3 schematically represents the two layers which have been applied to a surface in accordance with the invention.

Also, the non-porous, non-permeable layer prevents the occurrence of
30 carbon deposition on the metal surface under the porous layer upon heating in a gas atmosphere with carbon-containing molecules. Growth of carbon under the porous layer also greatly reduces bonding of this layer. The non-porous layer therefore protects the underlying material against undesired reactions with gases

at increased temperature or against corrosive action of liquids. This last can lead to a highly undesirable contamination of the reaction product. The underlying material can also exhibit undesired catalytic reactions by which selectivity is impaired. Finally, the underlying metal can react with a catalytically active component to form a non-active or less active compound. Thus, it is known that zeolites can take up metal ions of an underlying metal layer and thereby lose the catalytic activity. The use of such a non-porous intermediary layer thus constitutes an essential improvement of the prior art.

A non-porous, non-permeable layer applied to a solid surface, with a porous layer thereon is moreover of significance in the use of porous layers as catalytically active material or as support for one or more catalytically active components. In fact, catalysts generally lose activity during use, for instance by poisoning. In the case of suspended catalyst bodies, replacing the catalyst is extremely simple. In the case of a packed catalyst bed, too, the catalyst can be removed from the reactor and be replaced with a new catalyst charge, although this can be relatively labor-intensive. If the catalyst is applied as a thin porous layer on a special reactor packing, the consequence of deactivation of the catalyst might be that the entire, often costly reactor packing must be replaced. For the use of catalysts according to this invention, it is therefore required in many cases that the deactivated catalyst can be relatively readily removed from the surface of the reactor packing. According to the invention, this occurs by treating the reactor packing with an alkaline or acid liquid. With most metals, an alkaline liquid can be used because metals such as iron and nickel are resistant to alkaline liquids, while silicon dioxide-containing porous layers often dissolve readily in alkaline liquids. With a metal such as aluminum, however, this presents problems, since aluminum also dissolves in alkaline liquids, forming hydrogen. Because aluminum, in view of the low density, is especially attractive as reactor packing in larger reactors, protection of the aluminum is highly desirable. Therefore, according to a special embodiment of the invention, the substrate on which the catalytically active layer is applied, is provided with a non-permeable ceramic layer which is resistant to either acid, or basic, or acid or basic solutions. According to the present state of the art, it is possible to manufacture enamel layers that are resistant to acid, to alkali, or to both. As noted above,

acid-resistant enamel is obtained by incorporating *inter alia* titanium dioxide into the enamel. Resistance to strongly acid liquids is achieved by also incorporating fluorine, which, according to the invention, is readily possible by impregnation.

Lye-resistant enamel types contain zirconium dioxide often together with fluorine,

5 which, according to the invention, can also be readily included in non-porous, non-permeable layers according to the invention. Also known according to the prior art are enamel types that are resistant to both acid and lye. According to the invention, such materials are also readily applicable as thin layers on metal substrates. The starting point is a thin layer of silicone rubber, which is
10 subsequently pyrolyzed in air, whereby a porous layer of silicone dioxide is formed. This layer is impregnated with the components of the desired enamel, whereafter the thus covered surface is heated, preferably in a non-oxidizing gas atmosphere, at such a high temperature that a chemically homogeneous, non-porous, non-permeable layer is obtained.

15 Onto the desired non-porous, non-permeable layer, the porous layer of catalyst support material can be applied according to the known prior art. The most obvious option is to apply the porous layer by dip-coating or spin-coating. Excellent results have also been achieved by applying onto the surface of the non-permeable layer a layer of a suitable compound, such as silicone rubber,
20 titanium and zirconium compounds as the ammonium salt of a chelate with lactic acid of a titanate or a chelate of diethyl citrate of a zirconate, and subsequently pyrolyzing the layer.

 In certain cases, for instance in catalytic oxidations, it is of importance to provide the catalytically active material thermostably in a finely divided form
25 in a porous layer of a suitable catalyst support material. Surprisingly, it has now been found that a particularly thermostable fine division can be obtained by dissolving a suitable compound of the catalytically active metal, generally a precious metal, in the solution of the elastomer. Very good results have been obtained with acetic acid salts of palladium and platinum. However, also
30 organometallic complexes, such as acetyl acetonate complexes, are found to be highly satisfactory. As appears from measurements with X-ray photoelectron spectroscopy, a relatively large part of the precious metal, after pyrolysis and further sintering of the ceramic layer, is present at the surface.

Through the decomposition of silicone rubber or titanium and zirconium compounds as the ammonium salt of a chelate with lactic acid of a titanate or a chelate of diethyl citrate of a zirconate, layer thicknesses of about 5 mm can be achieved. This involves the successive application of layers of a thickness of about 1 mm. In many cases, however, it will be desired to use thicker porous layers. The thickness of the porous layer at which no transport impediments in the porous layer occur yet, depends, as noted above, on the rate of the catalytic reaction, on the diffusion coefficients of the reactants and the reaction products, and on the diameter of the pores. Since in the gas phase the diffusion coefficients are a factor of 100 higher than in the liquid phase, in gas phase reactions preferably somewhat thicker porous layers in which the catalytically active component(s) is/are provided will be employed. In relatively slow reactions in the liquid phase, a thickness of 50 mm can be utilized without this giving rise to transport impediments. It will be clear that the application of 50 layers, with requisite intermediate calcination to remove the organic constituents, is extremely laborious.

Surprisingly, it has now been found that a thin porous layer of a thermostable oxide which is strongly bonded onto a solid surface, is capable of eminently anchoring ceramic particles, such as used as catalyst support. 'Thin' in this connection is understood to mean a layer thickness of about 1 mm. Examples of thermostable oxides are silicon dioxide, titanium dioxide and zirconium dioxide. According to a special embodiment of the invention, therefore, a porous layer of a thermostable oxide is applied to the non-permeable layer according to the invention, on which a relatively thick catalytically active layer according to the known prior art has been applied. As discussed above, such layers of the support, which may or may not be priorly loaded with the catalytically active component or a precursor thereof, can be applied by dip-coating. Accordingly, in accordance with the invention, a support which may or may not be loaded with the active material, is applied to the porous intermediary layer by dip-coating in a suspension of the finely divided material. Through dip-coating, layers of a thickness of 50 mm or more can be applied. Figure 4 schematically represents such a composite layer.

The application of zeolite crystals on a solid substrate is of great practical significance. The transport in the relatively narrow pores of zeolites

proceeds slowly, so that small crystallites are eminently suitable for catalytic reactions. This applies to gas-phase reactions, but especially also to liquid-phase reactions. Now, the synthesis of zeolites leads indeed to small crystallites. In some zeolites, crystallites or strongly agglomerated crystallites of about 1 to 10 mm are
5 obtained, whereas in other zeolites, such as zeolite-b, much smaller crystallites, viz. smaller than 0.1 mm are formed upon synthesis. In gas-phase reactions, however, a gas stream is to be passed through a catalyst bed. For this purpose, a fixed catalyst bed can be used, but in connection with the allowable pressure drop and the prevention of channeling, no bodies smaller than about 1 mm can be used.
10 In gas-phase reactions the catalyst can also be provided in a fluidized bed, but this requires the use of bodies of a diameter of 60 to 150 mm or greater. In liquid-phase reactions no small catalyst bodies can be used either, since crystallites smaller than 1 mm cannot be properly separated from the reaction product by filtration or centrifugation. It is therefore either endeavored to
15 synthesize larger zeolite crystallites, which is often a great problem, or extremely small zeolite crystallites are included in a so-called binder, silicon dioxide or silicon dioxide/aluminum oxide, after which the combination is formed into larger bodies. Processing the zeolite/binder combination to form wear-resistant bodies of dimensions of 3 to 10 mm, however, is technically cumbersome, while the binder
20 often impedes transport and can lead to poor selectivity. Also, the binder may react with the zeolite to form a non-active or less active compound. Zeolite crystallites applied to a solid substrate are therefore of great technical significance.

According to the invention, zeolite crystallites are used which have
25 been applied via a non-permeable, non-porous layer on a surface of suitable moldings. Preferably, such a zeolite layer is applied to the surface of a metal or an alloy.

In the synthesis of the zeolite crystallites, the starting point will generally be a layer of porous silicon dioxide applied to a ceramic or metallic
30 molding. Although in most cases a continuous non-permeable intermediary layer according to the invention is needed, it will suffice, in special cases where moldings of relatively inert materials are used, to use a porous silicon dioxide layer and to grow the zeolite crystallites therefrom. For a proper bonding of the

zeolite crystallites onto the surface, however, it is required that between the zeolite crystallites and the surface, a silicate layer be present which does not react to form zeolite. In that case, however, the intermediary layer does not need to be continuous.

5 According to the invention, the necessary ingredients for the zeolite synthesis that are not already present in the porous layer are impregnated in the pores of the zeolite. When, for instance, a 'template' molecule is necessary for the synthesis of the zeolite, a solution of this template is impregnated in the porous ceramic layer obtained by pyrolysis of the dried silicone elastomer layer. The
10 aluminum necessary for the synthesis of the zeolite will generally be provided in the porous layer by dissolving in the solution of the elastomer. Preferably, the volume of the solution of the ingredients of the zeolite synthesis, as described above, is chosen to be equal to the pore volume of the porous layer, which is preferably impregnated after evacuation. After the impregnation, the layer is
15 brought under the conditions required for the nucleation and growth of the zeolite crystallites. In general, hydrothermal conditions are required for this purpose. Especially in the case of metallic substrates, it is extremely simple to accurately set and maintain the temperature during the synthesis.

 As noted above, in many cases, during the zeolite synthesis, metal ions
20 from the metal or alloy surface will dissolve intermediately and be taken up by the zeolite. The result is a catalytically inactive or less active zeolite. In this connection, the non-porous, non-permeable layer between the solid surface and the zeolite layer is of great significance, since it prevents reaction of the underlying metal and hence deactivation of the zeolite.

25 In general, in the above method, only a part of the silicon dioxide layer is found to have been converted to strongly bonding zeolite crystallites. Since in many cases it is preferred to use a thicker layer of zeolite crystallites, the surface covered with porous silicon dioxide will mostly be introduced into a liquid which contains the ingredients for forming zeolite crystals. Surprisingly, it has been
30 found that the zeolite crystallites formed in the liquid preferentially deposit, firmly anchored, on the surface on which the porous silicon dioxide layer has been applied. According to the invention, therefore, the surface covered with porous

silicon dioxide is introduced into a synthesis solution of the desired zeolite, whereafter the zeolite synthesis is allowed to proceed.

It is surprising that in this way zeolite crystallites very strongly bonded to solid surfaces are obtained. It is possible, according to the invention, to allow the initial porous layer to react wholly or partly to form zeolite crystallites. The thickness of the layer initially applied, consisting substantially of silicon dioxide, determines the density of the zeolite crystallites on the surface. It is of great significance that the surface to be covered with zeolite crystallites does not need to be horizontally oriented during the zeolite synthesis. This makes it possible without any problem to cover complex reactor packings.

Characteristic of zeolite crystallites applied, according to the method of the invention, to solid ceramic or metallic substrates, is that a non-porous, non-permeable layer is present at the interface between the substrate and the zeolite crystallites. It is possible for this layer to comprise not much more than a few layers of atoms, but the layer is always present. As noted above, it is of great importance, for the purpose of replacing deactivated catalysts, that the catalytically active layers or the catalytically active particles can be readily removed, without the ceramic or metallic substrate being affected. Therefore, according to a preferred embodiment of the invention, the zeolite crystallites are applied to an alkali-resistant non-permeable intermediary layer.

Obviously, such a method can also be practiced with zeolites. This provides the advantage that the zeolite can be prepared separately. Since zeolites typically crystallize to (extremely) small particles, it is relatively easy to make a suspension of them which is suitable for applying the zeolites to a surface covered with a silicon dioxide layer which may or may not be porous. In all of these cases, in accordance with the invention, between the catalytically active layer and the substrate a non-permeable, non-porous layer is present. It has been found that a porous silicon dioxide layer applied to the non-porous layer strongly increases the bonding of the zeolite layer.

Surprisingly, it has been found that for the purpose of application to electrically conductive surfaces, such as metal surfaces, electrophoresis is eminently suitable to apply support particles which may or may not be loaded with catalyst, or small catalyst particles. According to a preferred embodiment of

a method according to the invention, such a layer is applied through electrophoresis. The metal or alloy surface has priorly been covered with a non-porous, non-permeable layer, on which preferably a porous layer has been provided to improve bonding. A preferred embodiment of the catalytically active materials according to the invention therefore concern catalytically active porous layers applied to electrically conductive surfaces having a thickness up to about 50 mm, while between the metal or the alloy a thin (less than about 1 mm) non-porous layer and preferably a thin (less than about 1 mm) porous layer for improving the bonding is present. Figure 4 schematically represents the structure of the system. In general, in the electrophoresis, the starting point will be a suspension of particles having dimensions of less than 1 mm to about 10 mm. Obviously, it is possible to start from particles of a suitable support material and, after application to the surface, to anchor the catalytically active component or components in the layer. Also, the support particles can be priorly loaded with (a precursor of) the catalytically active component(s) and bonding these particles to the surface by electrophoresis. In a special embodiment of the invention, the layers are provided on structured metal surfaces, such as static mixers. In this case, a very good contact is obtained between a gas phase and a liquid phase or between two liquid phases.

Preferably, layers of zeolites or synthetic clay minerals which can be used as solid acid catalysts, of a thickness of more than 1 mm are applied to metal or alloy surfaces by electrophoresis. Zeolites are generally negatively charged, so that the metal surface to be covered needs to be brought to a positive voltage to enable deposition of the zeolite on the surface. Clay minerals too can be eminently deposited on metal or alloy surface by electrophoretic route.

In particular catalytic reactions which proceed in a liquid phase, it is of importance to keep the empty space between the catalytically active surfaces as small as possible. This is the case, for instance, if in the liquid phase itself unwanted reactions may proceed. According to the invention, a catalytically active layer of a thickness of about 50 mm at a maximum is applied to non-porous particles of dimensions of about 0.1 mm to about 10 mm. Surprisingly, it has been found that small metal particles having dimensions of about 0.1 mm to about 1 cm are eminently suitable for this purpose. Applied to the metal particles, in

accordance with the above methods, are a bonding layer and a porous layer containing the catalytically active component. When it is desired to pass a liquid stream at a relatively high rate in upward direction through a bed of metal particles loaded in such a manner, it is attractive to use relatively heavy metal particles. It may also be advantageous to use ferromagnetic metal particles and to
5 fix these particles with an inhomogeneous magnetic field in the reactor.

According to a special embodiment of the invention, therefore, use is made of metal particles having dimensions of about 0.1 to about 10 mm, covered with a layer, which may or may not be porous, in which or on which the
10 catalytically active component is present. A more special embodiment of the invention concerns ferromagnetic metal particles. Such ferromagnetic bodies which are fixed in a reactor by an inhomogeneous magnetic field or which can be separated from the liquid by an inhomogeneous magnetic field.

Electrophoretically covering small metal particles with a catalyst support layer can be done by using a fluidized bed of the metal particles. In that
15 case, the particles are held in floating condition by a liquid stream, while one or more electrodes make contact with the bed of the particles. According to a preferred embodiment of the invention, ferromagnetic particles are used which by means of an inhomogeneous magnetic field are held in floating condition in the
20 liquid in which the electrophoresis is being carried out.

Especially in reactions in which a liquid phase is involved, but also in gas phase reactions in which compounds having a higher boiling point occur, a porous surface with wide pores is attractive. In that case, a relatively thick porous layer can be used without the occurrence of transport impediments, so that the
25 catalytically active surface area per unit volume can be relatively great. Transport impediments can often lead to poor selectivities of the catalytic reaction. Now, it is known that from small metal particles, carbon fibrils can be allowed to grow, which yield such an open structure with wide pores.

Surprisingly, it has been found that providing metal particles from
30 which carbon fibrils can grow, in a porous layer of a support material applied to a solid surface, makes it possible to grow carbon fibrils which are firmly attached to the solid surface. Catalytically active materials can be applied to the carbon fibrils according to the known prior art. According to a special embodiment of the

invention, therefore, a solid surface is used on which carbon fibrils have been grown from a porous layer of a conventional catalyst support material, on which carbon fibrils catalytically active material has been provided.

According to a special method according to the invention, by
5 electrophoresis, a layer of a suitable support is provided on a surface on which priorly a firmly anchored porous layer has been deposited, which applied support has priorly been loaded with particles or a precursor of particles from which carbon fibrils can grow, or which applied support has been loaded with a precursor
10 of particles from which carbon fibrils can grow only after it has been applied to the surface, whereafter carbon fibrils are grown from the particles and finally a catalytically active material is applied to the carbon fibrils. In growing the carbon fibrils, the conditions will generally be chosen such that upon termination of the growth process the metal particles from which the fibrils grow have been encapsulated by carbon. In this case, the small metal particles will be incapable of
15 exhibiting any unwanted reactions with the liquid to be treated.

The choice of the chemical composition of the bonding layer to be applied to the metal surface, and the thicker porous layer of catalytic support material applied thereto, depends on the liquids which are to be processed after applying the catalytically active component. In the case of alkaline liquids,
20 preferably use will be made of a bonding layer and a support layer of titanium dioxide or zirconium dioxide. When processing acid liquids, preferably a non-porous bonding layer of silicon dioxide will be applied to the metal surface and then a catalyst support layer, likewise of silicon dioxide.

Such a surface loaded with carbon fibrils is also eminently suitable for
25 applying an ion exchanger thereto. The ion exchanger can be used as catalyst, but it is also attractive as an ion exchanger, because a relatively large fraction of the ion exchanger can be utilized due to good accessibility. Ion exchangers applied to carbon fibrils grown on the surface of materials are therefore part of the invention. Preferably, such carbon fibrils loaded with ion exchangers are applied
30 to surfaces of static mixers.

The invention will be elucidated with reference to the figures.

Figure 1 Schematic picture of a protective layer applied to a solid surface. (a) substrate, preferably a metal or an alloy; (b) protective layer.

Figure 2 Schematic picture of a surface covered with an non-porous, non-permeable protective layer on which a catalytically active component is provided. (a) substrate, preferably a metal or an alloy; (b) protective layer; (c) catalytically active material.

5 Figure 3 Schematic representation of a solid surface covered with a non-porous, non-permeable layer on which a porous layer with a catalytically active component is provided. (a) substrate, preferably a metal or an alloy; (b) protective layer; (c) porous layer in which catalytically active material (d) is provided.

10 Figure 4 Schematic representation of a solid surface covered with a non-porous, non-permeable layer (a), a porous bonding layer (b) and a porous layer (c) in which the catalytically active component (d) is provided.

15 Figure 5 Stainless steel plate covered with clay mineral by electrophoretic route. Recording with a Philips XL 30 FEG scanning electron microscope.

Figure 6 Higher magnification of a stainless steel plate covered with clay mineral by electrophoretic route. Recording with a Philips XL 30 FEG scanning electron microscope.

20 Figure 7 Carbon fibrils grown on a stainless steel plate after being covered with silicon dioxide and aluminum oxide. In the aluminum oxide, the nickel particles were present from which the carbon fibrils were grown through decomposition of methane.

The invention is elucidated with the following examples.

25

Preparation of porous ceramic layers based on silicon dioxide having added thereto aluminum oxide, titanium dioxide or zirconium dioxide.

30 The starting material was silicone rubber in the form of a commercial product, viz. Bison, "transparent", based on polydimethyl siloxane. This material was dissolved in diethyl ether. To the obtained solution was added aluminum sec-butoxide (ACROS), titanium isopropoxide (Jansen Chimica), or zirconium isopropoxide (Fluka). The concentration of silicone rubber in the solution was 6 to

10% by weight. With aluminum, a series having different Si/Al ratios was prepared, viz. $\text{Si}_{99}\text{Al}_1$, $\text{Si}_{70}\text{Al}_{30}$, $\text{Si}_{50}\text{Al}_{50}$, $\text{Si}_{35}\text{Al}_{65}$, $\text{Si}_{50}\text{Al}_{50}$, and $\text{Si}_{35}\text{Al}_{65}$. The titanium dioxide- and zirconium dioxide-containing silicon dioxide preparations contained Si/Ti and Si/Zr ratios of 80/20.

5 After pyrolysis at 873K, the pore volume of the material was determined as a function of the Si/Al ratio. While the pure silicon dioxide exhibited a pore volume of about 0.2 ml/g, the pore volume increased to 1.4 ml/g at an Al fraction of 0.2, to decrease at higher Al fraction to about 0.4 ml/g. The accessible surface area, determined by nitrogen adsorption according to the BET
10 theory, increased from 100 m²/g for pure silicon dioxide to 580 m²/g for an Al fraction of 0.75, then to decrease again to about 300 m²/g for pure aluminum oxide.

For preparations with Si/Al, Si/Ti and Si/Zr ratios of 80/20, the accessible surface area was determined as a function of the temperature. The samples were held at the different temperatures for 3 hours. For all three
15 preparations the surface area of 200 to 260 m²/g after calcining at 873K gradually decreased to 70 to 180 m²/g after calcining at 1173K. The material with zirconium dioxide was found, after calcining at 1173K, to exhibit the highest surface area. While pure silicon dioxide can be readily sintered at about 1073K to form a non-permeable layer, it is necessary, with increasing contents of aluminum, zirconium
20 or titanium, to heat at considerably higher temperatures. The content of aluminum, titanium or zirconium is selected depending on the temperature at which the material covered with a protective layer is to be used.

The material with $\text{Si}_{99}\text{Al}_1$ was used to examine the density. To that end, the material was applied to stainless steel. A sample of the stainless steel,
25 without having been covered with a layer, was heated at 900°C in a thermobalance. A rapid weight increase showed that the material oxidized relatively fast. Analysis showed that the surface was covered with a high-porous mass of chromium oxide upon completion of the experiment. When on a similar plate of stainless steel a layer with the specified ratio of Si/Al had been applied,
30 which was subsequently sintered in an inert atmosphere at 1200°C, not any change in weight was observed after correction for change of the upward pressure upon increase of the temperature.

Application of ZSM-5 (MFI) zeolite crystallites on a stainless steel substrate.

- 5 In this case, the starting point was a layer of porous silicon dioxide prepared by applying silicone rubber to stainless steel and decomposition of the silicone rubber layer at 773K. As template molecule, the tetramethylammonium from CFZ (Chemische Fabriek Zaltbommel) was used. Together with NaOH the tetrapropylammonium was impregnated in the pore volume of the porous layer.
- 10 Subsequently, the zeolite was synthesized under hydrothermal conditions at 140°C. Figures 1 and 2 give at two different magnifications a picture with secondary electrons of the resulting surface. It is clear that the surface is homogeneously covered with zeolite crystallites.

15 **Application of a layer of clay to a stainless steel plate**

- This involves the application of a synthetic clay mineral, saponite, which can function as an acid catalyst. The stainless steel plate to be coated, having dimensions of 1x2.5 cm, is placed in a 200 ml beaker and connected with a
- 20 negative electrode. On opposite sides of the stainless steel plate, a negative platinum electrode is present. As a result, both sides of the stainless steel plate are covered with clay mineral.

 In the beaker, a clay suspension containing about 5 g of clay mineral is put into water. Using a magnetic stirrer, the clay is held in suspension.

- 25 For 16 hours, a voltage of 6.5 V was maintained across the electrodes, whereby a current strength of 0.1 to 0.2 A was established. Thereafter, about 8 mg of clay was found to have deposited on the plate. While the plate had previously exhibited an immeasurably small surface area, the surface after coating with the clay layer was 72 m² per gram of clay. The pore volume was 0.62 ml per gram of
- 30 clay. Both quantities were measured with equipment of Micromeretics through the adsorption of nitrogen at 77 K. Figure 5 shows a recording made with a

scanning electron microscope of the resultant stainless steel plate covered with clay minerals.

Application of a layer of clay to a stainless steel powder

5

The stainless steel powder was introduced into a cylindrical wire net of stainless steel of a diameter of 2 cm. Contact with the stainless steel particles was made with two electrodes. The cylinder was placed in a 200 ml beaker in which a platinum electrode was present. The clay suspension was recirculated by means of a peristaltic pump. To that end, the suspension was withdrawn under the cylinder and recycled to the top of the cylinder. Using a magnetic stirrer, the clay particles were held in suspension. Fig. 6 schematically represents the setup used.

For 16 hours, the electrophoresis was carried out in this way. The current strength was 0.1 to 0.2 A. In this period, 78 mg of clay was deposited on 1.3 grams of metal powder. The surface of the uncovered metal powder was immeasurably small, while after coverage the surface was 68 m² per gram. This surface was measured in equipment of Micromeretics with adsorption of nitrogen at 77 K. The pore volume of the clay layer was 0.06 ml per gram.

Application of carbon fibrils to a stainless steel surface

To a stainless steel plate of 1x2.5 cm, a layer of silicon dioxide was applied, of a thickness of about 0.7 μ m. This was done by dipping the plate in a solution of silicone rubber in ethyl acetate. After pyrolysis of the silicone rubber at 400° C the coated plate was held in an inert atmosphere (argon with 1% hydrogen) at 900° C for 16 hours. Then, by electrophoretic route, aluminum oxide was applied to the plate, having a specific surface area of 270 m² per gram. The procedure in the electrophoresis was analogous to that of the above example in which a stainless steel plate was covered with clay mineral. After calcination of the thus covered plates for 4 hours at 450° C and cooling to room temperature, 18.7 mg of aluminum oxide was found to have been deposited on the plate. Then

nickel oxide was applied by impregnation with a solution of nickel nitrate (3 molar $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and calcining at 450°C . Thereafter the nickel oxide was reduced in a hydrogen stream at 400°C . Carbon fibrils were grown from the nickel particles at 570°C in a stream of 10% by volume of methane in argon for 10 hours. Figure 7 is a scanning electron microscope recording of the carbon fibrils which are present on the surface.



CLAIMS

1. Non-porous, non-permeable protective ceramic layers of a thickness of less than 50 μm , preferably of a thickness of less than 5 μm , and still more preferably of a thickness of less than 1 μm , which are bonded to a substrate through an intermediary layer which contains ions of the surface to be covered,
5 while in the case of substrates consisting of metals or alloys, the oxide of the covered material is not demonstrable with X-ray diffraction.
2. Non-permeable ceramic layers according to claim 1, firmly anchored to ceramic or metallic substrates obtained through sintering of one or more porous layers applied by pyrolysis of elastomers containing substantially not exclusively
10 sulfur, carbon, hydrogen and oxygen, or through dip-coating or spin-coating of suspensions of the material to be applied, or by a combination of the two prior art methods mentioned.
3. Non-permeable ceramic layers according to claim 1 or 2, characterized in that the layers substantially consist of silicon dioxide.
- 15 4. A method for the manufacture of ceramic or metallic moldings covered with ceramic layers according to one or more of claims 1-3, wherein the eventual sintering to a dense, non-permeable layer is carried out in an inert atmosphere.
5. Non-permeable ceramic layers according to claims 1-4, wherein the melting or softening point of the material of the layer is controlled by
20 incorporation of controlled amounts of alkali metal ions, aluminum ions, zirconium ions or titanium ions.
6. Non-permeable ceramic layers according to claims 1-4, wherein the resistance to acids is set by incorporation of titanium dioxide, if necessary combined with fluorine ions.
- 25 7. Non-permeable ceramic layers according to claims 1-4, wherein resistance to alkaline liquids is obtained by incorporation of zirconium ions which may or may not be combined with tin ions or by incorporation of boron.
8. Manufacture of ceramic or metallic moldings covered with ceramic layers according to claims 1-7, wherein a thin layer of a solution of elastomers
30 which contain the desired components is applied to the bodies and after drying of

the layer pyrolysis is carried out, whereafter the porous layer obtained is sintered at a higher temperature preferably in an inert gas atmosphere.

9. Manufacture of ceramic or metallic moldings covered with ceramic layers according to claims 1-7, wherein the desired chemical composition is
5 obtained by impregnation of the porous layer obtained by pyrolysis of the dried elastomer layer, with solutions of the desired elements.

10. Manufacture of ceramic or metallic moldings covered with ceramic layers according to claims 1-7, wherein the desired chemical composition is
10 obtained by impregnation of exclusively the pore volume of the porous layer obtained by pyrolysis of the dried elastomer layer, with solutions of the desired elements.

11. Manufacture of ceramic or metallic moldings covered with ceramic layers according to claims 1-7, wherein the desired chemical composition is
15 obtained by deposition-precipitation of the desired elements in the porous layer obtained by pyrolysis of the dried elastomer layer.

12. Metallic moldings, in particular metal gauzes, having applied thereto a high temperature-stable non-permeable ceramic layer, on the surface of which catalytically active particles are deposited.

13. Ceramic or metallic molding on which first a protective non-porous,
20 non-permeable layer has been provided, while on the non-porous layer a porous ceramic layer has been deposited in which catalytically active components are present in finely divided form.

14. A ceramic or metallic molding according to claim 13, on which a non-permeable intermediary layer is provided which is resistant to acid or alkali, or
25 resistant to acid and alkali.

15. A metallic molding according to claim 13 or 14, wherein the metal consists of aluminum.

16. Application of porous layers according to claims 13-15, to non-porous, non-permeable layers by dip-coating or spin-coating or by applying a layer of a
30 suitable compound, such as silicone rubber, titanium and zirconium compounds as the ammonium salt of a chelate with lactic acid of a titanate or a chelate of diethyl citrate of a zirconate and subsequently pyrolyzing the layer.



* C L M S *



17. Thin (thickness about 1 μm) porous layer of a thermostable oxide provided on the non-permeable layer according to claims 1-11, on which porous layer a relatively thick catalytically active layer has been applied according to the prior art.
- 5 18. Ceramic or metallic moldings covered with zeolite crystallites applied in a controlled density, characterized in that at the interface of the zeolite crystallites with the substrate, a non-zeolitic silicon-containing intermediary layer which may or may not be continuous is present.
- 10 19. Zeolite crystallites applied to an alkali-resistant non-permeable intermediary layer present on a metallic or ceramic molding.
20. Application of zeolite crystallites according to claim 18 or 19, characterized in that a porous layer of silicon dioxide, in which, if necessary, aluminum is incorporated, is impregnated with the other ingredients needed for the zeolite synthesis and is subjected to the conditions needed for the zeolite synthesis.
- 15 21. Application of zeolite crystallites according to claim 20, characterized in that exclusively the pore volume of a porous layer of silicon dioxide, in which, if necessary, aluminum is incorporated, is impregnated with the other ingredients needed for the zeolite synthesis and is subjected to the conditions needed for the zeolite synthesis.
- 20 22. A method for the manufacture of moldings covered with firmly anchored zeolites, characterized in that a surface covered with porous silicon dioxide is introduced into a synthesis solution of the desired zeolite, whereafter the zeolite synthesis is allowed to proceed.
- 25 23. A method for the manufacture of moldings covered with firmly anchored zeolites, characterized in that on a surface covered with porous silicon dioxide, a layer of zeolite crystallites is provided by dip-coating.
24. A method in which support particles which may or may not be loaded with (a precursor of) an active component are provided on an electrically
- 30 conductive molding covered with a thin non-permeable, non-porous layer on which, if necessary, a thin porous layer has been deposited, characterized in that the support particles are provided on the molding by electrophoresis.



25. A method in which zeolite particles or particles of a clay mineral are provided on an electrically conductive molding covered with a thin non-permeable, non-porous layer on which, if necessary, a thin porous layer is deposited, characterized in that the zeolite particles are provided on the molding by electrophoresis.
26. Catalytically active layers which may or may not be porous, according to claims 1-3, 5-7, 13-15 or 17-19, provided on non-porous ceramic or metallic particles having dimensions of about 0.1 mm to about 10 mm.
27. Catalytically active layers which may or may not be porous, according to claim 26, provided on ferromagnetic particles.
28. Electrophoretic coverage of small metal particles with a catalyst support layer by carrying out the electrophoresis in a fluidized bed of the metal particles.
29. Electrophoretic coverage of ferromagnetic particles with a catalyst support layer, which particles are held by means of an inhomogeneous magnetic field in floating condition in the liquid in which the electrophoresis is carried out.
30. Metal or ceramic molding on which, from a porous layer of a conventional catalyst support material, carbon fibrils have been grown on which catalytically active material has been provided.
31. A method characterized in that through electrophoresis a layer of a suitable support is applied to a surface on which priorly a firmly anchored porous layer has been deposited, wherein the support applied has priorly been loaded with particles or a precursor of particles from which carbon fibrils can grow, or has only after being applied to the surface been loaded with a precursor of particles from which carbon fibrils can grow, whereafter carbon fibrils are allowed to grow from the particles and finally a catalytically active material is applied to the carbon fibrils.