METHOD FOR PRODUCTION OF CATALYTIC SCREENS

Catalytic screens for ammonia combustion with air oxygen in reactors normally used for this purpose are produced by applying a thin layer of a catalytically active metal onto another, catalytically inactive support material. As the carrier of the catalytically active metal micro-expanded metal made of a suitable type of steel, preferably stainless steel with a high content of nickel, heat-resistant steel and the most preferably of Kanthal or Megaply is used. To achieve optimum efficiency of ammonia oxidation more individual catalytic screens produced according to invention are put on each other. The catalytic layer consists of platinum, rhodium and palladium applied preferably with the cold dynamic spray method, which ensures the required adhesion of catalytically active metals to the micro-expanded metal and excellent surface resistance. The cold dynamic spray method also enables changing the portions of individual active metals in the layer. The arrangement of catalytic screens with different ratios of the applied metals serves the purpose of increasing the efficiency, reducing the emissions of undesired compounds and reducing losses of platinum in the course of using the catalyst.
Method for production of catalytic screens

Technical Field

The invention relates to the production of catalytic screens, in particular for ammonia oxidation for the purpose of production of nitrous gases, which are further used especially for the production of nitric acid and hydrocyanic acid.

Background Art

According to the state of the art the method for production of nitric acid is based on the classical Ostwald principle of ammonia oxidation dated 1902 and subsequent absorption of a nitrous oxide in water. From the point of view of achieving satisfactory conversion the most important step is the exothermic reaction \( \Delta H = -247 \text{ kJ/mol} \) \( 4\text{NH}_3 + 50_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \) (I). Satisfactory conversion of ammonia is achieved under the atmospheric or increased pressure at the temperatures of 600 - 950\(^\circ\)C with the use of a platinum-based catalyst. At present, the range of temperatures of 820 to 950\(^\circ\)C is typically used at a pressure of up to 1.2 MPa. Subsequently, in the course of cooling of gaseous products nitrogen oxide is further oxidized to nitrous dioxide in a secondary air stream in accordance with the formula \( 2\text{NO} + \text{O}_2 \leftrightarrow 2\text{NO}_2 \) (II). The reaction is reversible while higher yields of \( \text{NO}_2 \) are achieved in such a way as e.g. described in the US patent No. 6 264 909, which discloses the possibility of increasing the efficiency of oxidation by quick transformation of nitrogen oxide from the gaseous phase into an aqueous solution enriched with \( \text{HNO}_3 \) with the use of homogeneous catalysis. The reaction produces a solution containing trivalent nitrogen: \( 4\text{NO} \) (g) + \( 2\text{HNO}_3 \) (aq) \( \rightarrow 3\text{N}_2\text{O}_3 + \text{H}_2\text{O} \) (III). It is the trivalent nitrogen that plays the role of the homogeneous catalyst. The oxidation with molecular oxide to \( \text{NO}_2 \) in the liquid phase is then easier and having higher yields.

Nitrogen dioxide or its dimer then comes in contact with water in the counter-current way and reacts to nitric acid and nitrogen oxide in accordance with the formula \( 3\text{NO}_2 + \text{H}_2\text{O} \leftrightarrow 2\text{HNO}_3 + \text{NO} \) (IV).
The method for the production of hydrocyanic acid is analogous to the production of nitric acid. The method is based on the Andrußow partial oxidation of a mixture of methane and ammonia platinum-catalyzed, which uses the formula \( \text{CH}_4 + \text{NH}_3 + 1.5\text{O}_2 \rightarrow \text{HCN} + 3\text{H}_2\text{O} \) (V). The reaction is generally carried out under the pressure of 0.1 - 0.3 MPa and the temperature of 1100 - 1200°C. The mutual conditions of the reactants as well as the other conditions of the reaction are mentioned in the US patent No. 3 104 945 or in the German patent DE 1282209.

In both the above mentioned processes catalytic screens with platinum as the main active component are used as the catalyst. Originally, pure platinum was used for these processes. Later, rhodium started to be added to improve the mechanical and catalytic properties. At present, screens made of Pt/Rh alloys, 90/10, 92/8 and 95/5 (in per cent of weight) are normally used. In some cases as e.g. trapping flying particles of Pt palladium is added to the alloy.

In accordance with the state of the art catalytic screens produced are made of wires from the corresponding alloy of precious metals with the wire diameter of approx. 0.06 - 0.08 mm. As regards the method for the production of the catalytic screen several methods have been designed differing especially with the shape and layout of the wire meshes. The oldest method for the production of screens is weaving. Although woven screens were improved several times in the past (see e.g. the document GB 2 062 485 or the document GB 2 062 486), their production is being abandoned at present due to their excessive weight, time requirements of the production, low flexibility and the high effect of surface shielding in the places where wires cross each other.

A specific improvement of the properties was brought by mechanically crocheted screens or knitted screens disclosed e.g. in the US patent No. 6 073 467, or in the international patent application published as WO 92/02301, which deal with increasing the active surface of wires that gets in contact with the streaming gases. US 6 073 467 suggests a method of screen knitting with the use of special mesh shapes to form a 3D structure with improved mechanical properties and more intense contact of the reactants with the active surface.
An example of the currently most widespread method for the production of catalytic screens may be a catalytic system for a medium-pressure reactor for the production of nitric acid with the burner diameter of 3 m and the daily production capacity of 250 t of 100% HNO₃/day. For the operation with the maximum useful life of the catalytic screens of one year a set of catalytic screens is produced, incl. pieces for trapping platinum particles on palladium. The total weight of precious metals contained in these screens will exceed 20 kg of Pt, nearly 1.5 kg of Rh and over 7 kg of Pd. 425 km of wires are produced from alloys of the above mentioned metals with a wire-drawing machine. The wires are further inserted in a knitting machine that produces fabric with the required shape and mesh size. Subsequently, circular screens with the required diameter are cut out of the fabric and the edges of the screens are reinforced by pressing or welding. Then, the screen activation stage follows, when the hitherto smooth surface of the wires is roughened chemically to increase the surface. The whole production process shows high requirements for time and technology, to say nothing of the losses of produced wires caused by cutting of the final shape of the screens. The method for the production of catalytic screens for HCN reactors is completely identical from the technological point of view.

In all the types of currently produced catalytic screens the Pt/Rh/(Pd) alloy fulfils both the function of the active component and the supporting structural material. Here it is necessary to point out that in the course of the life of the screen a relatively thin layer of metal gets in contact with the reacting gases and can fulfil its catalytic function.

So the state of the art shows that there is a need to develop a method for production of catalytic screens leading to economies of precious metals while these screens should have as low as possible production costs and maximum catalytic efficiency in the course of the whole life of the screen.

**Disclosure of Invention**

In comparison with the above mentioned methods for the production of catalytic screens the method for the production of catalytic screens according to the
invention brings up to 70% saving of the quantity of precious metals necessary to achieve the required catalytic effect in the course of the life of the catalytic screen.

The proposed system also makes the production considerably easier and shortens the production of a catalytic screen by abandoning the use of costly and slow weaving and knitting machines and at the same time it is not necessary to produce PtRh(Pd) wire in a lengthy and costly way.

The subject-matter of the invention deals with a method for the production of catalytic screens containing an active layer on the basis of precious metals comprising Pt, Rh, Pd while the active catalytic layer is formed by spraying of the above mentioned precious metals, their alloys or their mixtures onto the surface of a catalytically inactive support material with holes in the form of especially a grid, mat or mesh.

The invention covers complete removing using precious-metal wires and their replacement with a sprayed Pt/Rh/(Pd) alloy layer on a metallic carrier that does not show any catalytic properties itself, but mainly fulfils the function of a mechanical and structural carrier of the entire catalytic surface.

The advantage of the proposed method is that the task of the structural element that determines and maintains the shape of the screen, the size and distribution of its holes is taken over by a catalytically inactive, i.e. considerably cheaper carrying material.

As the structural material for the carrier of the catalytic layer you can preferably use heat and corrosion resistant steel or alloys of the Kanthal (72.5 % Fe, 20 % Cr, 5 % Al, 2.5 % Co) or Megapyr type (65 % Fe, 30 % Cr, 5 % Al) or other heat and corrosion resistant alloys.

The carrier of the sprayed layer of the above mentioned material with required heat and chemical resistance forms a mesh of regular holes of a defined shape and equal size that put up minimum resistance to the stream of the air-ammonia mixture and at the same time ensure the required contact time of the reactants with the active surface. For this purpose any woven or knitted mesh material can be used, advantageous micro-expanded metal made of a suitable type of steel as e.g. stainless steel having a high content of nickel with the thickness of the
initial sheet of 0.05 - 3.00 mm, preferably 0.12 - 0.20 mm, with meshes with a polygonal shape, advantageously rhombic, square, hexagonal or circular with a size of especially 0.10 - 5.00 mm, preferably 0.65 - 0.85 mm. The shape and size of the holes are selected on the basis of individual needs of the particular catalytic reactor.

Rhombic meshes, square meshes, hexagonal meshes, circular meshes are selected with regard to the technical parameters of the particular reactor, i.e. especially the working pressure, production capacity expressed in tons of 100 % HNO₃ per day, geometry of the burner and the flow of gaseous media through the layer.

Various sizes and shapes of the meshes have a principal influence on streaming characteristics as e.g. the mean contact time of the reactants with the active surface, the thickness of the laminar sub-layer in case of a turbulent character of the stream, the size of the shielding zone of the air-ammonia mixture stream in places under the outflow edges of the meshes and in particular the total amount of pressure loss generated by the flow of gases through the catalytic screen.

Depending on the above mentioned individual characteristics of the reactor you can further select whether the catalytically active sprayed layer will be applied on both sides or one side of the catalytically inactive support, which is especially preferable in reactors with high flows speeds, which means that there are relatively large shielded areas on the bottom sides, i.e. outflow sides of one-sided screens.

For the method for the production of catalytic screens herewith disclosed in accordance with the invention more ways of spraying the metallic layer on the base made of a different metal can be used. It is for example the case of the flame spraying, plasma spraying, or cold dynamic spray methods. With these methods the applied powder particles are accelerated to a speed in the range of 300 - 1500 m/s.

However, the cold dynamic spray method can be preferably applied. The cold dynamic spray method ensures high-speed fixation of small, non-melted particles of metallic powder with the mean diameter of particles selectable usually in the range of 1 to 120 micrometers, preferably in the range of 5 to 50 micrometers. These particles are first mixed with pre-heated gas (air, He, N₂, etc.) and
subsequently accelerated to a supersonic speed in the range of 500 to 1500 m/s, preferably 600 to 1000 m/s, by passing through a Lavall nozzle in general. The impact of particles with a sufficient kinetic energy on the target surface causes their plastic deformation, which will cause their immediate adhesion while the mechanical strength of the bond is comparable to detonation welding, which ensures excellent resistance of the surface.

Changes of the size of the applied particles are used to modify the total catalytically active surface and to reduce losses of platinum particles. The total thickness of the applied layer is calculated individually for the needs of the particular reactor and is adapted with the selection of the arm shift speed of the spraying robot. The total thickness of the catalytic layer is selected in such a way to achieve the required level of NH\textsubscript{3} conversion throughout the total time of one production campaign and at the same time to keep the residual weight of platinum not used for the reaction to the minimum at the end of the campaign. This effect cannot be achieved with the use of classical catalytic screens based on precious-metal wires.

To increase NH\textsubscript{3} conversion, to reduce emissions of undesirable compounds or to entrapment flying Pt particles on screens with a higher proportion of palladium you can put sprayed screens on each other in more layers with different ratios of applied metals, similarly to woven, knitted or crocheted wire screens.

With regard to the fact that catalysts of virtually any shape can be produced by the method of spraying a layer on catalytically inactive support material in accordance with the invention, these catalytic screens can be installed in existing reactors, for example for oxidation of ammonia without the need to adapt and modify their design.

The use of sprayed layers of catalytically active metals based on precious metals comprising Pt, Rh, Pd on an inactive support in comparison with wire screens has the possibility of performing in-situ repairs of the catalyst. Repairs can be performed e.g. in cases of the sprayed screen being locally damaged by a catalytic poison (which is detected in all types of screens during operation visually by delimited places with a lower temperature, i.e. with a darker colour). Such a place can be repaired after the shutdown of the reactor by shot blasting of the
affected place with alumina powder and spraying a new layer with the use of a mobile spraying unit.

A similar blasting procedure is applied after the end of the life of the screen, when the removal of the active layer leads to a reduction of the costs of refining of precious metals in comparison with screens made of wires where before the entire refining the whole material of the screen must be melted into an ingot or granules, which represents high energy demands.

Best Mode for Carrying Out of the Invention

The purpose of the following examples of the invention is to provide more detailed information about the principle of the invention.

However, embodiments disclosed in these examples cannot be in any case interpreted as a limiting scope of the invention that is defined with the attached claims.

Example 1

A method according to the invention of application of a sprayed layer on an inactive metallic support a set of catalytic screens was produced for a small nitric acid (HNO₃) unit having a reactor with the following parameters:

- Diameter of the burner on the screens: 1500 mm
- Temperature on the screens: 820 ºC
- Operating pressure: 400 kPa
- Production capacity: 70 t (100 % HNO₃)/day
- Total production per 1 campaign: 21,000 t (100 % HNO₃)

Required minimum conversion of NH₃ at the end of the campaign 96 %

For the above mentioned reactor a set of 3 catalytic screens was produced with the active layer consisting of Pt/Rh 95/5 % as well as 2 screens with a 100% Pd layer to entrapment platinum particles.
All the screens had the total diameter of 1500 mm with a pressed-in edge without holes with the width of 25 mm. As the supporting structure a micro-expanded metal grid was used with the thickness of 0.16 mm, made of a Kanthal alloy with non-rolled rhombic meshes with the size of 0.8 x 0.7 mm and bridges with the width of 0.16 mm.

In the case of the three catalytic Pt/Rh 95/5% screens 3,430 g of Pt/Rh 95/5 % with the mean size of particles of 50 micrometers were applied on the support with the cold dynamic spray method with the use of filtered air as the carrying gas and the pre-heating temperature of 700°C. The spraying was both-sided in the case of the first screen while the other two screens were subject to single-sided spraying.

In the case of the two screens for trapping Pt on Pd 1,840 g of 100% Pd with the mean size of particles of 50 μm were sprayed with the cold dynamic spray method, also with the use of air as the carrying gas and at the carrying gas pre-heating temperature of 700°C. A single-sided layer was applied on both the trapping screens.

The above mentioned screens can be used similarly for reactors used for the production of HCN.

Comparative example

In the case of using classical, at present most widespread knitted screens made of precious-metal wires for their production for the identical above mentioned reactor it would be necessary to use 9,500 g of Pt, 600 g of Rh and 3,500 g of Pd to ensure the same efficiency of the reaction and the same life of the catalyst.

Example 2

For the above mentioned reactor a set of 3 catalytic screens with the active layer consisting of Pt/Rh 95/5 % and 2 screens with a 100% Pd layer for trapping platinum particles was also produced, but with the flame spray method with the use of a thick wire as the source of necessary metals instead of using the cold dynamic spray method. The other parameters of the screens as the used micro-
expanded metal, diameter of the screens, the size and shape of the meshes, etc. remained the same as in the above mentioned example. The catalytically active layer was formed on the inactive support layer by spraying at the temperature of 3000 °C with the use of acetylene-oxygen flame and the outflow speed of 180 m/s. On the three Pt/Rh screens 3,670 g of PtVRh 95/5% were deposited while for the two palladium screens 1,970 g of 100% Pd were used.

Example 3

For the above mentioned reactor a set of 3 catalytic screens with the Pt/Rh active layer and 2 trapping palladium screens was produced. In all the screens the same ratio of precious metals were maintained as in example 1. In the case of the three catalytic Pt/Rh 95/5% screens 3,950 g of Pt/Rh 95/5% with the mean size of particles of 80 micrometers were applied on the inactive support the cold dynamic spray method with the use of filtered air as the carrying metal and at the pre-heating temperature of 700 °C. The first screen was subject to two-sided spraying while the other two ones to single-sided spraying.

In the case of the two screens for trapping Pt on Pd 2,12O g of 100% Pd with the mean size of particles of 80 µm were sprayed with the cold dynamic spray method, also with the use of air as the carrying gas and at the carrying gas pre-heating temperature of 700 °C. A single-sided layer was applied on both the trapping screens.

In contrast to the above mentioned examples 1 and 2 in this case as the support material micro-expanded metal made of heat-resistant austenitic steel, normally use in the power industry, i.e. with the content of 18 % of Mn and 9 % of Cr was used. The used micro-expanded grid had the thickness of 0.15 mm, non-rolled circular meshes with the size of 0.9 mm and bridges with the width of 0.18 mm. Due to a higher diameter of the meshes, their shape and also a higher mean size of the applied particles it was necessary to increase the weight of the applied metals to achieve the same efficiency of conversion as in example 1.

Example 4
For the above mentioned reactor a set of 3 catalytic screens with the active Pt/Rh layer was produced with the cold dynamic spray method of deposition of powder materials while in this case a homogenized mixture of pure powder Rh and pure powder Pt was used at the inlet. In contrast to example 1 the ratio of the components of Pt 98% / Rh 2% of weight was selected. The mean size of particles of 80 micrometers and the pre-heating temperature of 700 °C were maintained. The first screen was sprayed on both sides, the other two ones on one side. In this case the inactive support was represented by a micro-expanded metal grid with the thickness of 0.16 mm with non-rolled rhombic meshes with the size of 0.8 x 0.7 mm with bridges having the width of 0.16 mm. The material of this grid was the Megapyr alloy on the basis of FeCrAl.

**Industrial Applicability**

Catalytically active layers of pure platinum or platinum enriched with rhodium or palladium and applied by spraying especially on a grid made of catalytically inactive material can be used in reactors for catalytic oxidation of gaseous reactants at temperatures up to 1000 °C under the normal or increased pressure. In accordance with to the invention catalysts produced are first of all suitable for the production of hydrocyanic acid or nitric acid by ammonia combustion.
CL A I M S

1. A method for the production of catalytic screens containing an active layer based on precious metals comprising Pt, Rh, Pd, characterized in that the catalytically active layer is formed by spraying of the above mentioned precious metals, their alloys or their mixtures on the surface of a support consisting of a catalytically inactive material with holes, particularly in the form of a grid, mat or mesh.

2. The method for the production according to claim 1, characterized in that the catalytically inactive material of the screen support comprises heat and corrosion resistant steel or alloy of the Kanthal or Megapyr type or another heat and corrosion resistant alloy not made of precious metals.

3. The method for the production according to claim 1 or 2, characterized in that the catalytically inactive support material is micro-expanded metal.

4. The method for the production according to claim 3, characterized in that the thickness of the inactive support material is 0.05 to 3.00 mm, preferably 0.12 to 0.20 mm.

5. The method for the production according to any of the previous claims 1 to 4, characterized in that the shape of the holes in the catalytically inactive support material is circular, polygonal, preferably square, rhombic or hexagonal.

6. The method for the production according to claim 5, characterized in that the diameter of the holes in the catalytically inactive support material is 0.10 to 5.00 mm, preferably 0.65 to 0.85 mm.

7. The method for the production according to any of the previous claims 1 to 4, characterized in that the shape of the holes in the catalytically inactive support material is elliptical, semilunar or parallelogramic, preferably trapezoidal.

8. The method for the production according to any of the previous-claims 1 to 7, characterized in that the catalytic active layer on the surface of the screen
support is formed by deposition of powder materials with the cold dynamic spray, flame spraying or plasma spraying method, preferably the cold dynamic spray method.

9. The method for the production according to any of the previous claims 1 to 8, characterized in that the catalytic active layer is applied on one side or both sides of the screen support surface.

10. The method for the production according to any of the previous claims 1 to 9, characterized in that the size of the active catalytic surface is carried out through controlled changes of the size of the sprayed particles of the above mentioned precious metals.

11. The method for the production according to any of the previous claims 1 to 10, characterized in that the powder material is pure powder metal or a mixture of pure powder metals.

12. The method for the production according to any of the previous claims 1 to 10, characterized in that the powder material are alloy metal powders.

13. The method for the production according to any of the previous claims 1 to 12, characterized in that the size of the particles of the applied powder material is in the range of 1 to 20 micrometers, preferably 5 to 50 micrometers.

14. The method for the production according to any of the previous claims 1 to 13, characterized in that the speed of individual particles of the powder material is 300 to 1500 m/s, preferably 600 to 1000 m/s.