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(54) Catalysts for the dehydrogenation of ethylbenzene to styrene
Katalysatoren zur Dehydrogenierung von Ethylbenzol zu Styrol
Catalyseurs pour la déshydrogénation d’éthylbenzène en styrène

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(73) Proprietor: SÜD CHEMIE MT S.R.L.
20123 Milano (IT)

(72) Inventors:
• Rubini, Carlo
  22020 San Fermo Della Battaglia (IT)

(74) Representative: Modiano, Guido, Dr.-Ing. et al
Modiano & Associati SpA
Via Meravigli, 16
20123 Milano (IT)

(56) References cited:
EP-A- 0 591 572
US-A- 5 023 225

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Description

[0001] The present invention relates to catalysts in the form of hollow granules having a specific geometric shape and suitable for the dehydrogenation of ethylbenzene to styrene.

[0002] A previous and currently pending application of the Applicant discloses catalysts having a complex geometric shape, for example a hollow cylindrical shape with a circular or multilobed transverse cross-section with through holes at the various lobes, obtained by compression-molding of powders (tableting), using a lubricant applied to the walls of the molding chamber and to the plungers of the mold for lubrication.

[0003] The resulting catalysts are characterized by constant size parameters, high abrasion- and breakage-resistance characteristics, and very narrow pore radius distribution.

[0004] By virtue of the above mentioned type of porosity and of the high ratio between the geometrical area and the volume of the particles, the catalysts allow to considerably reduce the pressure drop that occur in a fixed-bed reactor and to significantly improve the activity and selectivity of the catalyst.

[0005] In patent literature concerning catalytic dehydrogenation of ethylbenzene to styrene, the interest has almost always been directed towards improving and optimizing the chemical composition in order to achieve ever more satisfactory performances. The improvements are generally obtained by varying the composition as regards the main components or by using different promoters.

[0006] Limited attention has been given so far to the geometry of the catalyst.

[0007] The importance of the shape can be directly correlated to the pressure used in the processes. Since the dehydrogenation reaction is accompanied by an increase in volume, a pressure reduction facilitates the shifting of the equilibrium towards the products (styrene and hydrogen), with a consequent improvement of the conversion. The possibility of modifying the shape of the catalyst so as to allow operation at a lower pressure (thus also reducing the pressure drop in the catalyst bed) is therefore desirable.

[0008] Furthermore, the dehydrogenation reaction is carried out in the presence of steam to reduce the partial pressure of styrene to shift the equilibrium towards the formation of styrene.

[0009] In order to solve this problem, two modifications have been adopted as regards the shape:

1) the granule diameter has been increased (to 5 mm) without altering its length. This has solved the problem only to a very limited extent, since a decrease in the pressure drop has indeed been achieved, owing to the reduced bulk density (and therefore owing to an increase in the void fraction), but at the same time the geometric surface exposed to catalysis has decreased. The result of these two contrasting effects has been a reduction in performance.

2) a three- or five-lobed geometric shape has been introduced. A slight improvement has been achieved in this case. However, one should bear in mind that the lobed shape has the drawback that powder forms more easily, since the lobes are weaker fracture points with respect to the solid cylindrical shape.

[0010] Industrially, the process used for catalyst shaping is extrusion molding. It should be noted that this technologically simple process has a very important limitation: specifically, it does not allow to obtain complex geometric shapes, particularly hollow shapes.

[0011] As regards composition, catalysts for the dehydrogenation of ethylbenzene to styrene comprise iron oxide, oxides of alkaline or alkaline-earth metals, and other oxides chosen among cerium, molybdenum, tungsten, and chromium oxide.

[0012] The life of the catalysts can be improved by adding chromium oxide as a stabilizer. US Patent 3,360,597 discloses catalysts which contain 0.5-5% Cr₂O₃ next to 80-90% Fe₂O₃ and 9-18% K₂CO₃. The catalyst is prepared according to a process which entails the mixing in water of yellow iron oxide, chromium oxide, and potassium carbonate so as to obtain a paste from which the catalyst is obtained in the form of cylindrical granules by extrusion, drying, and calcination.

[0013] US Patent 5,023,225 discloses a catalyst for the dehydrogenation of ethylbenzene to styrene which is based on iron oxide, oxides of alkaline or alkaline-earth metals, and cerium, molybdenum, or tungsten oxide, characterized in that the yellow iron oxide is blended with small amounts of chromium oxide prior to molding the catalyst. The molding process is characterized in that the yellow iron oxide blended with chromium oxide is heated to 500-1000°C to be converted into red iron oxide before mixing the components in the form of a wet paste. Molding is performed by extrusion.

[0014] The dehydrogenation catalysts according to the invention are defined in the appended claims and have a hollow geometric shape (with one or more through holes) obtained by compression-molding (tableting) with a method in which the lubricant to be used is not dispersed in the bulk of the powder to be formed (bulk lubrication) but is applied to the walls of the molding chamber and to the plungers of the mold (external lubrication).

[0015] The resulting catalysts have, with respect to those prepared by using bulk lubrication, a higher porosity, a
narrower pore radius distribution, and reduced macroporosity. Porosity is generally between 0.15 and 0.35 cm³/g (determined by mercury absorption). The surface area is generally between 1 and 6 m²/g (determined by BET method). The pore distribution curve does not include macroporosity with an average pore radius of more than 50,000 Å. More than 50% of the porosity has an average radius of more than 600 Å. More preferably, the average radius is between 800 and 1800 Å.

[0016] The catalysts furthermore have constant size parameter values. Constancy of the size parameters instead cannot be obtained with molding processes that use internal lubrication, owing to considerable microcracks which occur on part or all of the catalyst particle, causing embrittlement and subsequent deformation thereof.

[0017] Because of these deformations, the compression-molding process which uses bulk lubrication has never been used in industrial practice for the production of hollow granular catalysts. It has furthermore been found that the catalysts according to the invention are characterized by mechanical properties, particularly by an axial ultimate tensile strength (in the direction of the axis of the holes), considerably higher than those of the corresponding catalysts obtained by bulk lubrication. The axial ultimate tensile strength is higher than 15 N/particle and is preferably between 20 and 80 N/particle. Abrasion-resistance is also high. The percentage of powder is generally less than 3%. In catalysts obtained by extrusion, abrasion-resistance is generally between 4 and 8% by weight. The catalysts according to the invention, by virtue of the fact that they are hollow, allow to achieve a higher conversion, for the same weight, with respect to solid-shaped catalysts.

[0018] Furthermore, the greater presence of voids provided by these catalysts allows to operate, for an equal fed flowrate, at lower process pressures than required when using solid-shaped catalysts.

[0019] The greater presence of voids allows to operate with steam/ethylbenzene ratios higher than those usable with the catalysts having a solid shape, thus obtaining increased conversion for an equal process pressure.

[0020] The steam/ethylbenzene weight ratio usable with the catalysts of the invention is higher than 1.5 and can arrive to 2.5 or more.

[0021] The presence of holes allows to work with a lower wall thickness than in solid-shaped catalysts and therefore to better use the catalytic mass. The minimum wall thickness that can be achieved with these catalysts is between 0.6 and 0.8 mm.

[0022] For the same weight, the catalytic mass that can be used with the catalysts according to the invention is at least 1.5 times higher than that of solid-shaped catalysts having a minimum diameter of 3 mm which is compatible with the mechanical performances for practical use.

[0023] The pressure drop observed with the three-lobed catalysts according to the invention is at least 1.3 times lower than that of solid-shaped catalysts for an equal exposed geometric surface.

The lubricants that can be used to prepare the catalysts according to the invention include solids and liquids capable of reducing the friction coefficient between the powder to be tableted and the parts of the tableter that make contact with said powder.

[0024] Examples of suitable lubricants are stearic acid and palmitic acid; alkaline and alkaline-earth salts of these acids, such as magnesium and potassium stearate; carbon black, talc, mono- and triglycerides such as glycerol mono-oleate and glycerol mono-stearate and paraffin oil, and perfluoropolyethers.

[0025] The liquid lubricants can be used as solutions or as disperse systems in dispersants.

[0026] The amount of liquid lubricant is generally between 0.025 and 25 mg per granule.

[0027] The solid lubricants can be applied by dusting the forming chamber and the plungers, that is to say, by covering them with a thin layer of lubricant powder conveyed continuously by a stream of air or other gas so as to achieve optimum dispersion of the solid.

[0028] The molding chamber and the plungers can be made of, or coated with, self-lubricating materials, such as polytetrafluoroethylene or ceramic material. This allows to avoid or reduce the use of lubricant.

[0029] The catalysts according to the invention preferably have a hollow cylindrical shape with one or more through holes. In the case of catalysts with two or more through holes, the axes are substantially parallel to each other and to the axis of the granule and are substantially mutually equidistant.

[0030] Preferably, the through holes have a circular cross-section. In the case of catalysts with three through holes, the axes form, relative to the transverse cross-section of the particle, the corners of a substantially equilateral triangle; said corners are orientated towards the points where the transverse cross-section makes contact with the circumscribed circumference. The lobes are preferably cylindrical and circular, identical to each other, and coaxial to the through holes.

[0031] The granules may also have a substantially triangular transverse cross-section with rounded corners.

[0032] The ratio between the pitch of the holes (i.e., the distance between their respective axes) and the diameter of said holes is preferably between 1.15 and 1.5 and more preferably between 1.3 and 1.4.

[0033] The ratio between the height of the particle and the pitch of the holes is preferably between 1.5 and 2.5 and more preferably between 1.7 and 2.3.

[0034] In the case of catalysts having a circular transverse cross-section, the ratio between the radius of curvature of each lobe and the pitch of the holes is preferably between 0.6 and 0.9, more preferably between 0.7 and 0.8.
Fe₂O₃ = 78%; K₂O = 12%; CeO₂ = 5%; MgO = 2%; WO₃ = 0.9%; MoO₃ = 2.1% cerium carbonate, or ammonium molybdate as precursors of the active components.

Potassium oxide is preferred among oxides of alkaline metals, whilst magnesium and calcium oxides are preferred among alkaline-earth ones. Cerium oxide is preferred among lanthanide-series oxides, and molybdenum oxide among group VI oxides.

Another representative composition, again expressed as a percentage of oxides by weight, is:

Fe₂O₃ = 74%; K₂O = 6%; CeO₂ = 10%; MgO = 4%; WO₃ = 6%

The catalysts having a non-uniform composition, obtained by surface deposition of promoter and stabilizing components on the granules, contain 40-95% iron oxide, 5-30% alkaline metal oxide, 0.05-4% alkaline-earth metal oxide, 0.1-10% oxide of an element of the lanthanide series, 0.05-4% chromium, molybdenum, or tungsten oxide.

The promoters and stabilizers, such as calcium, magnesium, chromium, molybdenum, and tungsten oxide, can be distributed within the mass of the granule or on its surface. Various methods can be used to provide the surface deposition of the desired components. For example, the component or components can be sprayed onto the granules during tableting after the external lubrication step.

In particular, potassium oxide, calcium oxide, magnesium oxide, cerium oxide, and chromium, molybdenum, tungsten and the temperature at which deposition is performed can be changed so as to ensure quick and complete evaporation and stabilizing oxides or salts of metals by means of a nebulizer. The concentration of the dispersion, the contact time, and the temperature at which deposition is performed can be changed so as to ensure quick and complete evaporation of the water or other dispersant fluid, in order to form a surface layer having a desired thickness, generally between 0.1 and 100 microns.

In terms of final composition by weight, expressed as oxides, the catalysts comprise 50-92% ferric oxide, 5-20% alkaline metal oxide, 0.5-14% alkaline-earth metal oxide, 2-10% oxide of elements of the lanthanide series, and 0.5-6% oxide of a metal of the sixth group of the periodic table.

Potassium oxide is preferred among oxides of alkaline metals, whilst magnesium and calcium oxides are preferred among alkaline-earth ones. Cerium oxide is preferred among lanthanide-series oxides, and molybdenum and tungsten oxides are preferred among group VI oxides.

It is possible to use for example ferric hydroxide, ferric nitrate or carbonate, potassium hydroxide or carbonate, cerium carbonate, or ammonium molybdate as precursors of the active components.

A representative but non-limitative composition is as follows, expressed as oxides by weight percentages:

Fe₂O₃ = 78%; K₂O = 12%; CeO₂ = 5%; MgO = 2%; WO₃ = 0.9%; MoO₃ = 2.1%

Another representative composition, again expressed as a percentage of oxides by weight, is:

Fe₂O₃ = 74%; K₂O = 6%; CeO₂ = 10%; MgO = 4%; WO₃ = 6%

The catalysts having a non-uniform composition, obtained by surface deposition of promoter and stabilizing components on the granules, contain 40-95% iron oxide, 5-30% alkaline metal oxide, 0.05-4% alkaline-earth metal oxide, 0.1-10% oxide of an element of the lanthanide series, 0.05-4% chromium, molybdenum, or tungsten oxide.

In particular, potassium oxide, calcium oxide, magnesium oxide, cerium oxide, and chromium, molybdenum, tungsten oxide, or ammonium molybdate as precursors of the active components.

The pressure used is generally higher than 100 kg/cm² and can reach 1000 kg/cm² or more.

It has furthermore been found, and this constitutes a further aspect of the present invention, that catalysts with mechanical characteristics, particularly axial ultimate tensile strength, which fall within those of the catalysts that can be obtained by molding with external lubrication can also be achieved by shaping using bulk lubrication, provided that the powder, prior to shaping, is subjected to heat treatments capable of ensuring that the decomposition reactions which occur with weight loss take place before the molding step. In this case, the internal lubricant is used in an amount that is less than 5% by weight.

The resulting mixture is subjected to a drying and/or calcining cycle at temperatures between 120 and 1000°C for a time that is sufficient to remove the water and the volatile decomposition products.
and tungsten oxides are preferred next to iron oxide.

[0054] Examples of preferred but non-limitative compositions are listed hereafter. The asterisk indicates the component that can be deposited on the surface.

<table>
<thead>
<tr>
<th>%Fe₂O₃</th>
<th>%K₂O</th>
<th>%CeO₂</th>
<th>%MgO</th>
<th>%CaO</th>
<th>%Cr₂O₃</th>
<th>%MoO₃</th>
<th>%WO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>78</td>
<td>12</td>
<td>5</td>
<td>2</td>
<td>0.09*</td>
<td>/</td>
<td>2.1</td>
<td>0.9</td>
</tr>
<tr>
<td>78</td>
<td>14</td>
<td>5</td>
<td>0.1*</td>
<td>/</td>
<td>/</td>
<td>2</td>
<td>0.9</td>
</tr>
<tr>
<td>74.5</td>
<td>16.1</td>
<td>9.6</td>
<td>4.0</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>5.8</td>
</tr>
<tr>
<td>78</td>
<td>12</td>
<td>5</td>
<td>2.9</td>
<td>/</td>
<td>/</td>
<td>2</td>
<td>0.1*</td>
</tr>
<tr>
<td>78</td>
<td>12</td>
<td>5</td>
<td>4</td>
<td>/</td>
<td>/</td>
<td>0.1*</td>
<td>0.9</td>
</tr>
<tr>
<td>78</td>
<td>14</td>
<td>5</td>
<td>2.8</td>
<td>/</td>
<td>/</td>
<td>0.1*</td>
<td>0.1*</td>
</tr>
<tr>
<td>78</td>
<td>12</td>
<td>5</td>
<td>4.6</td>
<td>/</td>
<td>0.1*</td>
<td>0.1*</td>
<td>0.1*</td>
</tr>
</tbody>
</table>

The reaction for the dehydrogenation of ethylbenzene to styrene is usually performed at 540 to 650°C at pressures which are higher, lower, or equal to the atmospheric pressure. Low pressures are preferred due to thermodynamic reasons, since they allow higher conversions for an equal temperature.

[0055] The following examples are provided to illustrate and not to limit the invention.

Analytical determinations

[0056] The axial ultimate tensile strength was determined according to ASTM D 4179/82; apparent density (tapped) was determined according to ASTM D 4164/82.

Comparison Example 1

[0057] A paste was prepared by mixing hydrated ferric oxide, cerium carbonate, magnesium carbonate, and tungsten oxide with an aqueous solution of potassium hydroxide, so as to obtain a final catalytic product having the following composition (expressed in % of oxides by weight).

<table>
<thead>
<tr>
<th>Oxides</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>76.1</td>
</tr>
<tr>
<td>K₂O</td>
<td>14.0</td>
</tr>
<tr>
<td>CeO₂</td>
<td>6.5</td>
</tr>
<tr>
<td>MgO</td>
<td>2.5</td>
</tr>
<tr>
<td>WO₃</td>
<td>0.9</td>
</tr>
</tbody>
</table>

[0058] The paste was extruded to form granules with a length of 5 mm and a diameter of 3.5 mm. The extruded granules were dried at 150°C for 16 hours and then calcined at 400°C for 2 hours. Some of the granules were calcined at 700°C for 2 hours. These granules constitute the catalyst 1.

Example 1

[0059] A second part of the granules prepared according to comparison Example 1 was ground and the powder was tableted, using stearic acid as external lubricant. The plunger and the cylindrical chamber of the tableter were coated with a thin layer of stearic acid, carried continuously by an air stream. Cylinders 4 mm long, with a through hole having a diameter of 2 mm, were tableted. The pressure used was 500 kg/cm². The cylindrical granules were calcined at 700°C for 2 hours.

[0060] This is catalyst no. 2. The axial ultimate tensile strength of this catalyst was 13.4 N/particle.

Example 2

[0061] A second part of the granules prepared according to comparison Example 1 was ground and tableted (with
external lubrication using stearic acid) in a three-lobed shape with three parallel through holes having an inside diameter of 1.3 mm, with a wall thickness of 0.8 mm, a circumference radius of 2.5 mm, and a height of 5 mm. The holes were located at the corners of an equilateral triangle. The tablets were calcined at 700°C for 2 hours.  

This is catalyst no. 3. The axial ultimate tensile strength of this catalyst was 20.9 N/particle.

**Example 3**

A catalyst having the following composition by weight, expressed as oxides, was prepared with the method of comparison Example 1:

Fe₂O₃=74.5%; K₂O=6.1%; CeO₂=9.6%; MgO=4.0%; WO₃=5.8%

Fe₂O₃ in the red spheroidal form was used as Fe₂O₃. K₂O was introduced as KOH.

Calcination was performed at 800°C for 4 hours.

This is catalyst no. 4.

**Example 4**

Part of the granules prepared according to Example 3 was ground and tableted according to the method of Example 2 so as to obtain three-lobed granules with three holes, having the characteristics specified in Example 2.

Mg stearate was used instead of stearic acid as external lubricant.

The axial ultimate tensile strength of this catalyst was 32 N/particle; 38% of the volume was formed by pores having a radius of 600 to 800 Å, 11% by pores having a radius of 800 to 1000 Å, 12% by pores having a radius of 1000 to 2000 Å, and 6% by pores having a radius of 2000 to 4000 Å.

There were no macroporosities with a radius of more than 50000 Å.

The surface area of the catalyst was 4.9 m²/g; porosity was 0.17 ml/g.

This is catalyst no. 5.

**Example 5**

Catalysts no. 1, 2, 3, 4, and 5 were tested in a steel reactor with an inside diameter of 35 mm. In each test, 200 cm³ of catalyst were placed in the reactor and supported with a steel grille. Tests at 570°C, 590°C, and 610°C were conducted for each catalyst; in these tests, water vapor and ethylbenzene, preheated to the above temperatures, were passed through the catalytic bed with a water/ethylbenzene ratio of 2.4 by weight; the output pressure was 1.05 atm and the hourly spatial velocity of the ethylbenzene was 0.5. Samples of the reaction products were collected over 2 hours after the system had been stabilized for at least 20 hours for each condition. The percentages of conversion and molar selectivity are listed in the following table.

<table>
<thead>
<tr>
<th></th>
<th>Temperature(°C)</th>
<th>Conversion %</th>
<th>Selectivity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat. 1 BD=1.08</td>
<td>570</td>
<td>50.31</td>
<td>93.3</td>
</tr>
<tr>
<td></td>
<td>590</td>
<td>62.47</td>
<td>91.34</td>
</tr>
<tr>
<td></td>
<td>610</td>
<td>74.62</td>
<td>88.05</td>
</tr>
<tr>
<td>Cat. 2 BD=1.01</td>
<td>570</td>
<td>54.66</td>
<td>93.34</td>
</tr>
<tr>
<td></td>
<td>590</td>
<td>64.85</td>
<td>91.52</td>
</tr>
<tr>
<td></td>
<td>610</td>
<td>75.34</td>
<td>88.73</td>
</tr>
<tr>
<td>Cat. 3 BD=0.857</td>
<td>570</td>
<td>55.12</td>
<td>93.53</td>
</tr>
<tr>
<td></td>
<td>590</td>
<td>65.43</td>
<td>91.70</td>
</tr>
<tr>
<td></td>
<td>610</td>
<td>76.17</td>
<td>89.08</td>
</tr>
<tr>
<td>Cat. 4 BD=1.42</td>
<td>570</td>
<td>60</td>
<td>88</td>
</tr>
<tr>
<td>Cat. 5 BD=1.08</td>
<td>570</td>
<td>60</td>
<td>90.5</td>
</tr>
</tbody>
</table>

BD = apparent density in g/ml.
Claims

1. Catalysts in the form of granules having a definite cylindrical shape, provided with one or more through holes, usable in the dehydrogenation of ethylbenzene to styrene, comprising as components expressed as oxides ferric oxide as active component and as promoters oxides of alkaline and alkaline-earth metals, oxides of the lanthanide series, and tungsten oxides, obtained by compression-molding of powders of the precursors and the active component by using, for lubrication, a lubricant applied to the walls of the molding chamber and to the plungers of the mold.

2. Catalysts according to claim 1 having a porosity between 0.15 and 0.35 cm$^3$/g and wherein, in the pore radius distribution curve, over 50% of the pores have a radius of more than 600 Å and wherein there are no macroporosities with a radius of more than 50000 Å.

3. Catalysts according to claims 1 and 2 in the form of cylindrical granules with one or more through holes which are parallel to each other and to the axis of the granule.

4. Catalysts according to claims 1 and 2, in the form of multilobed granules with lobes which are coaxial to the through holes.

5. Catalysts according to claim 4, provided with three holes, wherein the ratio between the pitch of the holes and the diameter of said holes is between 1.15 and 1.5 and the ratio between the height of the granules and the pitch of the holes is between 1.5 and 2.5.

6. Catalysts according to claims 1 to 5 having an axial ultimate tensile strength (in the direction of the axis of the holes) of more than 15 N/particle.

7. Catalysts according to claim 6, wherein the ultimate tensile strength is between 20 and 80 N/particle.

8. Process for the dehydrogenation of ethylbenzene to styrene, wherein catalysts chosen among those according to the preceding claims 1 to 7 are used.

9. Process according to claim 8, wherein the weight ratio steam/ethylbenzene used in the dehydrogenation of ethylbenzene is higher than 1.5.

Patentansprüche

1. Katalysatoren in Form von Granulaten mit einer definierten zylindrischen Form, ausgestattet mit einem oder mehreren Durchgängen, die zur Dehydrierung von Ethylbenzen zu Styren verwendbar sind, umfassend als Komponenten, ausgedrückt als Oxide, Eisentrioxid als aktive Komponente und als synergetischen Verstärker Oxide von Alkali- und Erdalkalimetallen, Oxide der Lanthanoïden-Reihe und Wolframoxide, und die durch Druckformen von Pulvern der Vorstufen und der aktiven Komponente unter Verwendung eines Schmiermittels zum Schmieren, das auf die Wände der Formkammer und auf die Druckstempel der Form aufgetragen wird, erhalten wurden.

2. Katalysatoren nach Anspruch 1 mit einer Porosität zwischen 0,15 und 0,35 cm$^3$/g und wobei in der Porenradius-Verteilungskurve, über 50 % der Poren einen Radius von mehr als 600 Å aufweisen und wobei es keine Makroporositäten mit einem Radius von mehr als 50.000 Å gibt.

3. Katalysatoren nach den Ansprüchen 1 und 2 in Form von zylindrischen Granulaten mit einem oder mehreren Durchgängen, die parallel zu einander und zur Achse der Granulate liegen.

4. Katalysatoren nach den Ansprüchen 1 und 2 in Form von mehrfach gelappten Granulaten mit Ausbuchtungen, die zu den Durchgängen coaxial liegen.

5. Katalysatoren nach Anspruch 4, die mit drei Löchern ausgestattet sind, wobei das Verhältnis zwischen dem Abstand der Löcher und dem Durchmesser der Löcher zwischen 1.15 und 1.5 und das Verhältnis zwischen der Höhe der Granulate und dem Abstand der Löcher zwischen 1.5 und 2.5 liegt.
6. Katalysatoren nach den Ansprüchen 1 bis 5 mit einer axialen maximalen Zugfestigkeit (in Richtung der Achse der Löcher) von mehr als 15 N/Teilchen.

7. Katalysatoren nach Anspruch 6, wobei die maximale Zugfestigkeit zwischen 20 und 80 N/Teilchen liegt.

8. Verfahren zur Dehydrierung von Ethylbenzen zu Styren, wobei Katalysatoren verwendet werden, die aus denen, die den vorhergehenden Ansprüchen 1 bis 7 entsprechen, ausgewählt wurden.

9. Verfahren nach Anspruch 8, wobei das bei der Dehydrierung von Ethylbenzen verwendete Gewichtsverhältnis Dampf/Ethylbenzen höher als 1,5 ist.

Rewendung

1. Catalyseurs sous la forme de granules ayant une forme cylindrique définie pourvue d’un ou plus de trous débouchants utilisables pour la déshydrogénation d’éthylbenzène en styrène comprenant comme composés sous forme d’oxyde l’oxyde de fer comme composant actif et comme promoteur des oxydes de métaux alcalins ou de métaux alcalino-terreux, des oxydes de la série des lanthanides et des oxydes de tungstène obtenus par moulage par compression à partir de précurseurs en poudre et des composés actifs en utilisant pour la lubrification un lubrifiant appliqué aux parois de la chambre de moulage et au piston du moule.

2. Catalyseurs selon la revendication 1, ayant une porosité comprise entre 0,15 et 0,35 cm³/g et dans lesquels, dans la courbe de distribution du rayon des pores, plus de 50% des pores ont un rayon de plus de 600 Å et dans lesquels il n’y a aucune macro-porosité dont le rayon est de plus de 50000 Å.

3. Catalyseurs selon les revendications 1 et 2 sous la forme de granules cylindriques ayant un ou plus de trous débouchants qui sont parallèles les uns aux autres et à l’axe de la granule.

4. Catalyseurs selon les revendications 1 et 2 sous la forme de granules multilobes avec des lobes qui sont coaxiaux aux trous débouchants.

5. Catalyseurs selon la revendication 4, pourvus de trois trous, dans lesquels le rapport entre l’entraîne des trous et le diamètre desdits trous est compris entre 1,15 et 1,5 et le rapport entre la hauteur des granules et l’entraîne des trous est compris entre 1,5 et 2,5.

6. Catalyseurs selon l’une quelconque des revendications 1 à 5 ayant une résistance limite à la traction axiale (dans la direction de l’axe des trous) de plus de 15 N/particule.

7. Catalyseurs selon la revendication 6, dans lesquels la résistance limite à la traction est comprise entre 20 et 80 N/particule.

8. Procédé pour la déshydrogénation d’éthylbenzène en styrène, dans lequel les catalyseurs utilisés sont choisis parmi ceux des revendications précédentes 1 à 7.

9. Procédé selon la revendication 8, dans lequel le rapport en poids vapeur/éthylbenzène utilisé dans la déshydrogénation d’éthylbenzène est supérieur à 1,5.