Mouldings consisting of pyrogenic mixed oxide and use thereof

This invention relates to mouldings based on pyrogenically produced mixed oxide, to a process for the production thereof and to the use thereof as a catalyst support or catalyst.

Pyrogenically produced oxides are distinguished by extreme fineness and a correspondingly elevated specific surface area, very high purity, spherical particle shape and the absence of pores. Due to these properties, there is increasing interest in pyrogenically produced oxides as supports for catalysts (D. Koth, H. Ferch, Chem. Ing. Techn. 52, 628 (1980)). In some cases, pyrogenic oxides are also used as a catalyst.

Since pyrogenically produced oxides are particularly finely divided, shaping them into catalyst supports or catalysts occasions some difficulties.

DE-A 31 32 674 discloses a process for the production of compression mouldings from pyrogenically produced oxides, in which silica sol is used as the binder.

DE-A 34 06 185 discloses a process for the production of compression mouldings, in which glaze frit powders are used as binder and glycerol as lubricant.

DE-A 39 12 504 discloses a process for the production of compression mouldings, in which aluminium stearate, magnesium stearate and/or graphite are used as lubricants and urea together with methylcellulose are used as pore formers.

These compression mouldings are offered for sale as Aerosil tablets no. 350, Degussa. They contain approx. 0.4 wt.% Mg.

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Mouldings based on pyrogenic oxides are known. EP-B 0 393 356 accordingly describes high purity mouldings based on pyrogenically produced silicon dioxide. These mouldings consist of > 99 wt.% of pyrogenically produced SiO_2 and have a low binder material content. The Examples describe the use of Mg and Al stearates.

DE-A 196 19 961 describes mouldings based on pyrogenically produced silicon dioxide. The purity of these mouldings has been increased to > 99.8 wt.% of SiO_2.

Documents EP-B 0 452 619, EP-B 0 394 677 and EP-B 0 327 723 describe mouldings based on pyrogenically produced titanium dioxide. These mouldings are differentiated inter alia by having a content of anatase, rutile, by purity, dimensions etc.. Titanium dioxide contents are stated as > 99 wt.%, > 99.5 wt.% and > 94 wt.%. In the latter case, the content of anatase is at least 50 wt.%, with the remaining 0-6 wt.% consisting of non pyrogenically produced SiO_2 and/or non pyrogenically produced Al_2O_3.

EP-B 0 327 721 describes mouldings based on pyrogenically produced Al_2O_3. Purity is stated as a content of 94-99 wt.% Al_2O_3. The remaining 1-6 wt.% are SiO_2. The SiO_2 fraction originates from kaolin, which is used during shaping of the aluminium oxide powder.

Mouldings based on pyrogenically produced ZrO_2 are furthermore known. These are described in the document EP-B 0 327 814. The purity of these materials is stated as > 92 wt.% of zirconium dioxide. In this case too, the remainder contains fractions of non pyrogenically produced SiO_2 and Al_2O_3. Small fractions of HfO_2, which is a natural impurity in ZrO_2, are also present.

Known mouldings based on pyrogenically produced oxide may be used as a catalyst or catalyst support. The elevated

purity and good mechanical and chemical properties play an important part in many applications.

It is furthermore known to modify the composition of the mouldings for particular applications by purposefully adding certain foreign elements. Examples of this are described in the document EP-A 0 723 810. Supports are mentioned which consist of SiO_2, the composition of which has been modified by impregnation with Al, Zr and/or Ti. Once the moulding had been impregnated, it was dried and calcined.

This known production method is highly elaborate, as modifying the base material by impregnation, drying and calcination makes substantial demands with regard to equipment and energy. Moreover, production times for modified mouldings are distinctly longer.

It is known to produce pyrogenic mixed oxides by simultaneously reacting at least two different metals in the form of volatile metal compounds, for example chlorides, in a H_2/O_2 flame. One example of such an oxide is the SiO_2/Al_2O_3 mixed oxide, which is produced by Degussa and sold under the name Aerosil® MOX 170. When producing Aerosil® MOX 170, a mixture of $SiCl_4$ and $AlCl_3$ is directly hydrolysed in a flame. Corresponding silanes, such as for example methyltrichlorosilane, trichlorosilanes etc. may also be used as a raw material instead of or in addition to the chlorides. (Degussa Technical Bulletin Pigments, No. 11: Basic Characteristics of Aerosil®, pages 37 and 11-12; AT-A 195 893; DE-A 952 891; DE-A 25 33 925; DE-A 27 02 896).

It is furthermore known to produce mouldings based on pyrogenically produced silicon dioxide/aluminium oxide mixed oxide (EP-B 0 327 815). These mixed oxides consist of at least 75 wt.% silicon dioxide and at most 25 wt.% aluminium oxide.

The present invention provides mouldings based on pyrogenically produced mixed oxide having the following physicochemical parameters:

External diameter	0.8-25 mm
BET surface area	5-400 m^2/g
Pore volume	0.2-1.8 ml/g
Fracture strength	5 to 350 N
Composition	At least two from the group SiO_2, Al_2O_3, TiO_2 and ZrO_2 in any desired combination, but with the exception of SiO_2/Al_2O_3 mixed oxides, in which > 75 wt.% of SiO_2 is present.
Other constituents	< 1 wt.%
Bulk density	250-1500 g/l

The mouldings according to the invention may be present as extruded mouldings, extrudates or tablets. They may assume the form of cylinders, cylinders having rounded end faces, spheres, rings, wagon wheels, miniliths or other shapes conventional for fixed bed catalysts.

The present invention also provides a process for the production of mouldings according to the invention based on pyrogenically produced mixed oxide having the following physicochemical parameters:

External diameter	0.8-25 mm
BET surface area	5-400 m^2/g
Pore volume	0.2-1.8 ml/g
Fracture strength	5-350 N
Composition	At least two from the group SiO_2, Al_2O_3, TiO_2 and ZrO_2 in any desired combination but with the exception of SiO_2/Al_2O_3 mixed oxides in which > 75 wt.% of SiO_2 is present.

Other constituents	< 1 wt.%
Bulk density	250-1500 g/l

which process is characterised in that pyrogenically produced mixed oxide is homogenised as desired with one or more compounds from the group methylcellulose, methylhydroxyethylcellulose, wax, magnesium stearate, aluminium stearate or polyethylene glycol with the addition of water, dried at a temperature of 70 - 150 °C, optionally comminuted to yield a powder, the powder is compression moulded to yield mouldings and heat treated for a period of 0.5 to 10 hours at a temperature of 400 to 1200 °C.

The mouldings according to the invention may be produced in stamping presses, eccentric presses, isostatic presses, extrusion presses, rotary presses or compactors.

Before pressing, in one particular embodiment of the invention, the mixture may exhibit the following composition:

50-90 wt.%	mixed oxide
0.1-20 wt.%	methylhydroxyethylcellulose, preferably 5-15 wt.%
0.1-15%	wax, preferably 5-12 wt.%
0.1-15%	polyethylene glycol, preferably 5-10 wt.%.

Fracture strength, specific total surface area and pore volume may be adjusted to a certain extent by varying the quantities of starting materials and the compression pressure.

The present invention also provides a process for the production of mouldings according to the invention based on pyrogenically produced mixed oxide having the following physicochemical parameters:

External diameter	0.8-25 mm
BET surface area	5-400 m^2/g
Pore volume	0.2-1.8 ml/g
Fracture strength	5-350 N
Composition	At least two from the group SiO_2, Al_2O_3, TiO_2 and ZrO_2 in any desired combination but with the exception of SiO_2/Al_2O_3 mixed oxides in which > 75 wt.% of SiO_2 is present.
Other constituents	< 1 wt.%
Bulk density	250-1500 g/l

which process is characterised in that pyrogenically produced mixed oxide is homogenised as desired with one or more compounds from the group methylcellulose, methylhydroxyethylcellulose, wax, magnesium stearate, aluminium stearate or polyethylene glycol with the addition of water, subjected to a kneading and shaping process, extruded, the extrudates are optionally chopped to the desired length by means of a chopping device, dried at a temperature of 70 - 150 °C, and heat treated for a period of 0.5 to 10 hours at a temperature of 400 to 1200 °C.

Any mixers or mills which permit good homogenisation, such as for example blade mixers, fluidised bed mixers, centrifugal mixers or air-swept mixers, are suitable for performing the process according to the invention. Particularly suitable mixers are those with which the material being mixed may additionally be compacted, such as for example plough bar mixers, pan mills or ball mills. Mixing and kneading may, however, also proceed directly in an extruder. The extrudates may also be produced in single or twin-screw extruders, extrusion presses as well as in compactors.

After homogenisation, the product may be largely dried at 70-150 °C, such that, after an optional comminution operation, a pourable powder is obtained.

The mouldings according to the invention may be used either directly as a catalyst or as a catalyst support. In the latter case, once produced, the mouldings may be brought into contact with a catalytically active substance and optionally be activated by suitable post-treatment.

The mouldings made from the pyrogenically produced mixed oxide produced according to the invention may in particular be used in olefin hydration processes.

The mouldings according to the invention exhibit the following advantages:

In comparison with the mouldings according to documents EP 0 723 810 A1 and EP 0 792 859 A2, production of the mouldings according to the invention is substantially simpler and makes reduced demands with regard to energy, time and equipment.

The mouldings according to the invention exhibit improved hydrothermal stability in hydration processes.

Catalysts are subject to ageing during service which results in a reduction in activity and/or selectivity. Deactivation is frequently due to a reduction in the specific surface area of the support caused by elevated temperatures.

The specific surface area of the support is closely associated with the pore structure thereof. Moreover, solids having an elevated surface area generally have a completely amorphous or predominantly amorphous structure, which has the tendency to transform into a thermodynamically stable state with crystallite growth and reduction in specific surface area.

It has been found that known catalyst supports containing silicon dioxide also undergo such ageing. Hydration conditions accelerate ageing. It is furthermore known that impurities, in particular alkali metals, promote the ageing of supports containing silicon dioxide under hydrothermal conditions (c.f. for example R.K. Iler in "The Chemistry of Silica", page 544, John Wiley & Sons (1979)).

The catalyst supports based on pyrogenically produced silicon dioxide described in EP 0 393 356 are also subject to ageing under hydrothermal conditions, wherein small pores combine to form larger pores with the loss of specific surface area. Initially, pore volume scarcely changes.

As described in EP 0 792 859 A2, ageing stability may be increased by adding Ti and/or Zr. In said patent, these elements are applied onto an SiO_2 moulding by impregnation, followed by drying and calcination. As already explained above, these additional stages demand time, energy and equipment.

The object of the present invention is accordingly to provide catalyst supports which exhibit improved ageing stability when used under hydrothermal conditions.

This object of stabilisation is better achieved by using catalysts which have an active component on a moulding according to the invention based on a pyrogenic mixed oxide.

The present invention furthermore provides a process for hydrating olefins to yield the corresponding alcohols in the presence of phosphoric acid or another active component, for example a heteropolyacid, as the catalyst on the moulding according to the invention based on pyrogenically produced mixed oxide.

A process in which the mouldings according to the invention based on pyrogenically produced mixed oxide may be used is described, for example, in document EP-A 0 578 441. In this process, water and ethylene are reacted at temperatures of between 225 and 280 °C and pressures of between 20 and 240 bar to yield ethanol. A molar ratio of water:ethylene in the range from 0.15 to 0.5 is used in this process. Catalyst loading, measured in grammes of water/ethylene mixture per minute and millilitre of catalyst, may be selected within the range from 0.01 to 0.1 g/(min × ml). Diethyl ether is formed as a secondary product in this reaction.

Isopropanol is produced by hydrating propylene under similar conditions, but at a somewhat reduced temperature in the range between 180 and 225 °C. n-Propanol is obtained as a secondary product in this reaction.

According to EP 0 578 441 A2 pellets of synthetic silicon dioxide having elevated fracture strength, elevated porosity and a low metallic impurity content are used as a known catalyst support for the phosphoric acid active component.

The use according to the invention is particularly advantageous for hydrating olefins. The stabilisation of the support is, however, also favourable for other catalytic reactions performed under hydrothermal conditions.

In the case of olefin hydration, phosphoric acid is applied as the active component onto the catalyst support. To this end, the support is immersed in an aqueous solution of phosphoric acid and impregnated therewith. Phosphoric acid solutions containing 15 to 85 wt.% of phosphoric acid, relative to the total weight of the solution, are used for this purpose.

One main application for the hydration of olefins is the hydration of ethylene to produce ethanol and diethyl ether and the hydration of propylene to produce isopropanol. Reaction conditions known from the prior art are used in these cases.

A further object of the present invention is to provide a catalyst which exhibits improved ageing stability when used under hydrothermal conditions.

This object is achieved by a phosphoric acid catalyst which contains 1 to 50 wt.% of H_3PO_4, relative to the total weight of the catalyst, on a moulding according to the invention. This catalyst is characterised in that the moulding based on pyrogenically produced mixed oxide has the following physicochemical parameters:

External diameter	0.8-25 mm
BET surface area	5-400 m^2/g
Pore volume	0.2-1.8 ml/g
Fracture strength	5 to 350 N
Composition	At least two from the group SiO_2, Al_2O_3, TiO_2 and ZrO_2 in any desired combination but with the exception of SiO_2/Al_2O_3 mixed oxides in which > 75 wt.% of SiO_2 is present.
Other constituents	< 1 wt.%
Bulk density	250-1500 g/l.

The catalysts according to the invention are produced by surface-modifying the mouldings with phosphoric acid as the active component. To this end, the support particles or mouldings are immersed in an aqueous solution of phosphoric acid and impregnated therewith, so filling the pore volume of the support particles with the phosphoric acid solution. Phosphoric acid solutions containing 15 to 85 wt.% of phosphoric acid, relative to the total weight of the

solution, are used for this purpose. Depending upon the particular pore volume of the support particles, said particles may be surface modified in this manner with 1 to 50 wt.% of H_3PO_4, relative to the total weight of the finished catalyst.

Mixed oxides are produced by injecting volatile metal compounds into a detonating gas flame of hydrogen and air. These metal compounds hydrolyse under the action of the water generated in the detonating gas reaction to yield metal oxides and hydrochloric acid. After leaving the flame, the metal oxide enters a so-called coagulation zone, in which the mixed oxide primary particles and primary aggregates agglomerate. The product, which at this stage is in the form of a kind of aerosol, is separated from the gaseous accompanying substances in cyclones and is then post-treated with moist hot air. The residual hydrochloric acid content may be reduced to below 0.025% by this process. Since, at the end of this process, the mixed oxide is obtained with a bulk density of only approx. 15 g/l, vacuum compaction may subsequently be performed, by means of which tamped densities of approx. 50 g/l and above may be established.

The particle sizes of the products obtained in this manner may be varied by means of the reaction conditions, such as for example flame temperature, hydrogen or oxygen content, the nature and quantity of the metal chloride substances, the residence time in the flame or the length of the coagulation section.

The BET surface area is determined with nitrogen to DIN 66 131. The pore volume is calculated from the sum of the micro-, meso- and macropore volumes. Fracture strength is determined using a model TBH 28 Erweka fracture strength tester.

Micro- and mesopores are determined by recording an N_2 isotherm and evaluating it in accordance with BET, de Boer and Barret, Joyner, Halenda.

Bulk density is determined in the conventional manner known to the person skilled in the art.

Macropores are determined using the Hg infiltration method.

Example 1

71.4 wt.% of pyrogenic SiO_2/TiO_2 mixed oxide
(70 wt.% SiO_2, 30 wt.% TiO_2)
12.9 wt.% of methylhydroxyethylcellulose
7.1 wt.% of wax
8.6 wt.% of polyethylene glycol

are compacted with the addition of water, dried at 90 °C, comminuted to yield a pourable powder and shaped into mouldings using an eccentric press. The green tablets are calcined for 6 hours at 750 °C.

Example 2

71.4 wt.% of pyrogenic SiO_2/TiO_2 mixed oxide
(82 wt.% SiO_2, 18 wt.% TiO_2)
12.9 wt.% of methylhydroxyethylcellulose
7.1 wt.% of wax
8.6 wt.% of polyethylene glycol

are compacted with the addition of water, dried at 100 °C, comminuted to yield a pourable powder and shaped into mouldings using an eccentric press. The green tablets are calcined for 6 hours at 700 °C.

Example 3

71.4 wt.% of pyrogenic SiO_2/TiO_2 mixed oxide
(91 wt.% SiO_2, 9 wt.% TiO_2)
12.9 wt.% of methylhydroxyethylcellulose
7.1 wt.% of wax
8.6 wt.% of polyethylene glycol

are compacted with the addition of water, dried at 100 °C, comminuted to yield a pourable powder and shaped into

mouldings using an eccentric press. The green tablets are calcined for 10 hours at 600 °C.

Example 4

71.4 wt.% of pyrogenic SiO_2/TiO_2 mixed oxide (91 wt.% SiO_2, 9 wt.% TiO_2)
12.9 wt.% of methylhydroxyethylcellulose
7.1 wt.% of wax
8.6 wt.% of polyethylene glycol

are compacted with the addition of water, dried at 100 °C, comminuted to yield a pourable powder and shaped into mouldings using an eccentric press. The green tablets are calcined for 6 hours at 750 °C.

Example 5

90.0 wt.% of pyrogenic TiO_2/ZrO_2 mixed oxide (94 wt.% TiO_2, 6 wt.% ZrO_2)
5.0 wt.% of methylhydroxyethylcellulose
2.0 wt.% of wax
3.0 wt.% of polyethylene glycol

are compacted with the addition of water, dried at 100 °C, comminuted to yield a pourable powder and shaped into mouldings using an eccentric press. The green tablets are calcined for 10 hours at 400 °C.

Example 6

92.6 wt.% of pyrogenic TiO_2/ZrO_2 mixed oxide (94 wt.% TiO_2, 6 wt.% ZrO_2)
0.9 wt.% of methylhydroxyethylcellulose
6.5 wt.% of wax

are compacted with the addition of water, dried at 100 °C, comminuted to yield a pourable powder and shaped into mouldings using an eccentric press. The green tablets are calcined for 10 hours at 400 °C.

The mouldings obtained according to Examples 1-6 exhibit the following physicochemical parameters:

Example	1	2	3	4	5	6
Tablet shape	Cylinders	Cylinders	Cylinders	Cylinders	Rings	Rings
External diameter x height x internal diameter (mm)	5x5	6x5.5	6x5.5	5x5	8x5x3	8x5x3
BET surface area (m^2/g)	86	101	209	191	44	46
Pore volume (ml/g)	0.69	0.59	0.83	0.72	0.34	0.42
Fracture strength (N)	21	34	37	66	15	12
Bulk density (g/l)	n.d.	610	505	n.d.	860	800

Investigation of ageing stability of catalysts according to the invention:

The ageing stability of the catalysts according to the invention and of a comparison catalyst according to the prior art under hydrothermal conditions is investigated by determining the pore structure of the aged catalysts, i.e. after impregnating the supports with phosphoric acid and hydrothermal ageing. Pore structure is determined by means

of mercury porosimetry. The unaged catalysts (according to the invention and comparison catalysts) have pores of between 0.01 and 0.05 μm.

The Figures show

Figure 1 Pore size distribution of an aged catalyst on the moulding according to the invention according to Example 1

Figure 2 Pore size distribution of an aged catalyst on the moulding according to the invention according to Example 2

Figure 3 Pore size distribution of an aged catalyst on the moulding according to the invention according to Example 3

Figure 4 Pore size distribution of an aged catalyst on the moulding not according to the invention according to Example 8.

The pore size distribution curves shown in Figures 1 to 4 reveal the differential penetration (intrusion) of the mercury as a function of pore diameter. Differential intrusion is stated in arbitrary units and the curves are in each case extended over the available area of the diagram.

Example 7

The catalyst supports from Examples 1, 2 and 3 are each immersed in a 60 wt.% H_3PO_4 solution and then exposed to a water vapour pressure of 15 bar and 350 °C in a high pressure apparatus for 40 hours. The pore size distribution of the aged catalysts is determined using Hg porosimetry.

Figures 1 to 3 are a graphical representation of the results. As may be seen from these Figures, pore enlargement has occurred since, as stated above, the unaged material has pores in the range from 0.01 to 0.05 μm.

Example 8 (Comparative Example)

A known compression moulding (catalyst support 350, Degussa, containing 0.4 wt.% Mg (elemental), BET surface area 180 m^2/g, bulk density 490 g/l, total pore volume 0.8 cm^3/g, tablets of diameter 6 mm and height 5.5 mm) is loaded with phosphoric acid (60 wt.%) and then exposed to a water vapour pressure of 15 bar and 350 °C in a high pressure apparatus for 41 hours. The pore size distribution of the aged catalyst is determined using Hg porosimetry. Figure 4 is a graphical representation of the results.

The hydrothermally aged supports exhibit a maximum of the pore size distribution at pore diameters of between 20 and 30 μm. The proportion of pores having a diameter of less than 10 μm is much lower than in the materials according to the invention in Figures 1 to 3. The materials according to the invention are thus distinctly more stable towards hydrothermal ageing.

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Patent Claims

1. Mouldings based on pyrogenically produced mixed oxide having the following physicochemical parameters:

External diameter	0.8-25 mm
BET surface area	5-400 m^2/g
Pore volume	0.2-1.8 ml/g
Fracture strength	5 to 350 N
Composition	At least two from the group SiO_2, Al_2O_3, TiO_2 and ZrO_2 in any desired combination but with the exception of SiO_2/Al_2O_3 mixed oxides in which > 75 wt.% of SiO_2 is present.
Other constituents	< 1 wt.%
Bulk density	250-1500 g/l.

2. Process for the production of mouldings according to claim 1 based on pyrogenically produced mixed oxide having the following physicochemical parameters:

External diameter	0.8-25 mm
BET surface area	5-400 m^2/g
Pore volume	0.2-1.8 ml/g
Fracture strength	5 to 350 N
Composition	At least two from the group SiO_2, Al_2O_3, TiO_2 and ZrO_2 in any desired combination but with the exception of SiO_2/Al_2O_3 mixed oxides in which > 75 wt.% of SiO_2 is present.
Other constituents	< 1 wt.%
Bulk density	250-1500 g/l

characterised in that pyrogenically produced mixed oxide is homogenised as desired with one or more compounds from the group methylcellulose,

methylhydroxyethylcellulose, wax, polyethylene glycol, magnesium stearate or aluminium stearate with the addition of water, dried at a temperature of 70 - 150 °C, optionally comminuted to yield a powder, the powder is compression moulded to yield mouldings and heat treated for a period of 0.5 to 10 hours at a temperature of 400 to 1200 °C.

3. Process for the production of mouldings according to claim 1 based on pyrogenically produced mixed oxide having the following physicochemical parameters:

External diameter	0.8-25 mm
BET surface area	5-400 m^2/g
Pore volume	0.2-1.8 ml/g
Fracture strength	5 to 350 N
Composition	At least two from the group SiO_2, Al_2O_3, TiO_2 and ZrO_2 in any desired combination but with the exception of SiO_2/Al_2O_3 mixed oxides in which > 75 wt.% of SiO_2 is present.
Other constituents	< 1 wt.%
Bulk density	250-1500 g/l

characterised in that pyrogenically produced mixed oxide is homogenised as desired with one or more compounds from the group methylcellulose, methylhydroxyethylcellulose, wax, polyethylene glycol, magnesium stearate or aluminium stearate with the addition of water, subjected to a kneading and shaping process, extruded, the extrudates are optionally chopped or crushed to a desired length, dried at a temperature of 70 - 150 °C, and heat treated for a period of 0.5 to 10 hours at a temperature of 400 to 1200 °C.

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4. Use of the mouldings according to claim 1 as a catalyst or catalyst support.

5. Phosphoric acid catalyst which contains 1 to 50 wt.% of H_3PO_4, relative to the total weight of the catalyst, on a shaped, inorganic support, characterised in that the support consists of a moulding according to claim 1.

6. Use of catalysts which contain an active component which is applied onto a moulding according to claim 1 for catalytic reactions under hydrothermal conditions.

7. Use according to claim 6 for hydrating olefins.

8. Use according to claim 7, characterised in that phosphoric acid is used as the active component.

9. Use according to claim 7, characterised in that a heteropolyacid is applied as the active component.

10. Use according to claim 8 or 9 for hydrating ethylene to produce ethanol and diethyl ether.

11. Use according to claim 8 or 9 for hydrating propylene to produce isopropanol.