Catalyst system for producing ketones from epoxides

The present invention relates to a catalyst composition comprising at least one precious metal and at least one mixed oxide comprising zirconium dioxide and silicon dioxide. Furthermore, its preparation and its use forms a subject-matter of the invention. Moreover, a process for producing ketones and a process for the synthesis of lactams are claimed.

The patent application EP-A-2772478 (US 2014/0249331) describes a process for producing a ketone from an epoxide using a mixture comprising at least one precious metal and at least one metal oxide as catalyst system, where the metal oxide comprises zirconium dioxide. Using pure zirconium dioxide as metal oxide, the epoxycyclododecane was able to be converted to cyclododecanone with yields of up to more than 96%.

Although this process provides the ketone in high selectivity, considerable amounts of catalyst, long reaction times and high temperatures are required, which has an adverse cost effect on any industrial process.

The aim now was to adapt the rearrangement of epoxides to ketones in such a way that the amount of catalyst or the reaction time can be reduced. Moreover, the ketone should be obtained in at least equally high selectivity and/or yield. Moreover, it would be a processing advantage if the temperature of the reaction could turn out lower than in processes of the prior art.

Catalyst compositions of the type specified at the start have now been found which are able to solve the problem.

The compositions comprise at least one precious metal and at least one mixed oxide, where the mixed oxide comprises zirconium dioxide and silicon dioxide. The mass ratio of zirconium dioxide to silicon dioxide in the mixed oxide is 86: 14 to 99.9: 0.1, preferably 90: 10 to 97: 3. The stated mass ratio excludes, for example, silicon dioxide doped with zirconium dioxide. The mass ratio is

calculated on the basis of the zirconium and silicon compounds used for the mixed oxide.

In a first embodiment, the precious metal is not supported (system I).

In a second embodiment, the precious metal is supported, where the support does not consist of the mixed oxide (system II). The term "does not consist of" thus in conclusion excludes a support which comprises 100% by weight mixed oxide, based on the total weight of the support. In a preferred embodiment, the support does not comprise the mixed oxide or consist of it. This preferred embodiment thus encompases both the case that the support does not consist of the mixed oxide, and also the case that the support does not comprise the mixed oxide. The last-mentioned case includes the limiting case that the support does not consist of the mixed oxide. Impurities up to 1% by weight mixed oxide, caused for technical reasons, based on the total weight of the support, are excluded.

The support of the precious metal is preferably selected from silicon dioxide, aluminium oxide, activated carbon or mixtures thereof, with silicon dioxide being preferred. The specific surface area of the mixed oxide, measured according to BET methods, is preferably 5 – 155 m^2/g.

In a third embodiment of the invention (system III), the mixed oxide cannot be preparable from organosilicon compounds. The specific surface area of the mixed oxide, measured according to BET methods, is 5 - 155 m^2/g and the precious metal is supported on the mixed oxide (the mixed oxide acts as a support). In this connection, the mixed oxide has a monomodal pore radius distribution. In this connection, it is preferred that the mixed oxide can be prepared from silicon dioxide which has a particle size of at least 100 nm.

The pore radius distribution can, for example, be influenced by the addition of pore formers. In this connection, the person skilled in the art can ascertain, by means of corresponding preliminary experiments, whether monomodal or

higher-grade distributions are obtained.

The pore radius distribution of the mixed oxides is determined by means of mercury porosimetry. Mercury porosimetry was measured on Pascal 440 and Pascal 140 devices from CE Instruments with a maximum pressure of 4000 bar in accordance with DIN 66133.

The three embodiments of the invention comprising the systems I, II and III are referred to as catalyst systems according to the invention.

Systems II and III are preferred catalyst compositions, with system II being particularly preferred. The advantage of system II is that support and precious metal, particularly in the case of continuous processes, can be separate from the mixed oxide. As a result of this, a separate reaction implementation is made possible. Moreover, the separation of the precious metal from the mixed oxide reduces the ageing of the precious metal (the selectivity is reduced with ageing).

The mixed oxide of systems I and II preferably has a BET surface area which is in the range of 5 – 155 m^2/g.

It is preferred that the BET surface area of the mixed oxides of the catalyst systems according to the invention is in a range from 80 to 150 m^2/g. The BET surface area is measured in accordance with DIN 66131 and DIN ISO 9277. A BET surface area above 155 m^2/g leads to a lower selectivity.

Surprisingly, the catalyst compositions according to the invention catalyse the formation of the ketones during the rearrangement of epoxide compounds. The ketone can be obtained in high yield and purity. Furthermore, it is possible to use smaller catalyst amounts compared to the prior art and/or realize shorter reaction times. Moreover, the reactions are catalysed at lower temperatures.

Catalyst compositions with mixed oxides outside of the specified mass ratio

exhibit significantly lower activities. Moreover, the selectivity of the ketone formation decreases during the rearrangement of epoxides.

In the context of the present invention, mixed oxide is understood as meaning a composition which comprises at least zirconium dioxide and silicon dioxide. Zirconium dioxide and silicon dioxide are not present in the mixed oxide as concrete compounds, but serve merely as a base for calculating the mass ratios. The mixed oxide is obtained by calcination. The mixed oxide therefore does not constitute a physical mixture of zirconium dioxide and silicon dioxide, but a chemical mixture comprising at least silicon and zirconium cations with a unique crystal structure. In this regard, a physical mixture which comprises at least the two oxides and has not been calcined does not constitute a mixed oxide for the purposes of the invention. Nor is zirconium dioxide–doped or coated silicon dioxide included.

The mixed oxide comprises zirconium dioxide and silicon dioxide or consists of these two oxides. The fraction of the sum of zirconium dioxide and silicon dioxide in the mixed oxide is preferably at least 20% by weight and preferably at least 30% by weight, particularly preferably 50% by weight and very particularly preferably 95% by weight, in each case based on the total weight of the mixed oxide. The mixed oxide particularly preferably consists of zirconium dioxide and silicon dioxide.

The mixed oxide of the catalyst system can have an average bulk density of from 0.5 to 2 g/cm^3. The bulk density is measured by firstly weighing an empty 1000 ml measuring cylinder. The mixed oxide is then poured in up to the 500 ml mark. The filled cylinder is weighed again, the weight difference between the filled and empty measuring cylinder giving the bulk density of the material in g/cm^3.

The catalyst compositions according to the invention comprise the mixed oxide. Moreover, a support for the precious metal can be present which does not consist of the mixed oxide (inert support, system II). Preferably, the support

does not comprise the mixed oxide or consist of it. The mixed oxide as support, and also the inert support, can be present as powders or as mouldings, preference being given to these supports as mouldings. It is likewise preferred that the mixed oxide is present as moulding if the mixed oxide does not function as precious metal support.

Suitable mouldings are beads, extrudates, tablets, granules and pellets. The conversion of powders to mouldings is described for example in chapter 9 "Shaping of Solid Catalysts" in the book "Synthesis of Solid Catalysts", ed K. P. de Jong, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany (2009).

The weight-based ratio of mixed oxide to precious metal for all catalyst systems can be 99.9: 0.1 to 50: 50, preferably 99.5: 0.5 to 80: 20 and preferably 99:1 to 90:10.

If the precious metal is supported (catalyst systems II and III), the fraction of precious metal, based on the total weight of precious metal and support, can be 0.01 to 5% by weight, preferably 0.05 to 2.5% by weight and preferably 0.3 to 2.0% by weight. The precious metal can be distributed on or within the support.

The precious metal of the catalyst system is preferably selected from ruthenium, rhodium, palladium, osmium, iridium, platinum and mixtures thereof, with ruthenium, palladium and platinum being preferred and ruthenium and palladium being particularly preferred and palladium being very particularly preferred. In the series of the three precious metals ruthenium, palladium and platinum, platinum is less suitable because of its comparatively low selectivity with regard to CDON. The precious metal can be present as powder (unsupported) or in supported form. The precious metals can be present as elemental metals or in the form of their oxides, preference being given to elemental metals.

The invention further provides a process for producing the catalyst composition

according to the invention. The composition comprises at least one precious metal and at least one mixed oxide. To produce the mixed oxide, firstly a mouldable mass is prepared which at least comprises a zirconium compound, silicon dioxide as solid and water. The mouldable mass is then calcined at a temperature of from 300 to 500°C, preferably 400 to 500°C. To produce the system III it is necessary that the silicon dioxide has a pore size d_{50} of at least 100nm. For the system III, it is preferred that no polymers selected from polyalkylene pyrrolidones such as polyvinylpyrrolidone, polyamines, polyacrylates, polyalcohols, polysiloxanes or mixtures thereof are added. As a result of this, a bimodal pore radius distribution is prevented from arising.

A silicon dioxide as solid is understood as meaning a powder which does not form a stable dispersion in water. The silicon dioxide as solid preferably has a particle size d_{50} of less than 500 μm. Preferably, the particle size is less than 500μm, this upper limit being determined by means of sieve analysis (mesh of 500μm; this upper limit, determined by means of sieve analysis, is consequently a maximum value and not an average value d_{50}). Likewise, the solid preferably has a particle size d_{50} of greater than 100 nm (for systems I and II). For all systems I, II and III, the particle size d_{50} is preferably greater than 500 nm and particularly preferably greater than 1μm. The particle size d_{50} will be ascertained by laser diffraction in accordance with ISO 13320:2009. For the measurement operation, solid (according to manufacturers instructions) is placed into the Scirocco 2000 dispersing unit of a Malvern Mastersizer 2000. The pressure selected is 1 bar and the measurement is carried out.

Colloidal solutions of SiO_2 such as Ludox (Grace Davison) and Köstrosol (CWK Bad Köstritz) are not preferred. These types of colloidal solutions generally comprise individual SiO_2 particles with a size d_{50} between 5 and 30 nm. In order to ascertain the particle size of SiO_2 in a colloidal solution, a Zetasizer of the nano line from Malvern is used. The measurement is carried out at room temperature.

Preferably, the silicon dioxide is produced by means of pyrogenic methods.

The process is known to the person skilled in the art, e.g. from the series of papers "Fine Particles" No. 11 (7th Edition, 2003), company journal of Degussa AG.

The zirconium compound is preferably selected from zirconium dioxide, zirconium hydroxide, zirconium acetate, zirconium nitrate, zirconium oxychloride, ammonium zirconium carbonate or mixtures thereof. Preference is given to using zirconium dioxide, zirconium hydroxide or mixtures thereof.

Zirconium hydroxide is understood as meaning zirconium(IV) hydroxide.

It is likewise preferred to select the zirconium compound from a mixture comprising A and B. In this connection, A comprises zirconium dioxide, zirconium hydroxide and mixtures thereof. B is selected from zirconium acetate, zirconium nitrate, zirconium oxychloride, ammonium zirconium carbonate and mixtures thereof. The fraction of zirconium from A is preferably at least 85 mol%, preferably at least 90 mol%, based on the sum of zirconium from A and B.

As a result of the calcination, the zirconium compounds are reacted at least partially to give zirconium dioxide. In this regard, zirconium compounds, apart from zirconium dioxide itself, are referred to as precursors.

Preferably, the person skilled in the art selects time conditions through which at least 50 mol%, preferably at least 90 mol%, particularly preferably 95 mol% and very particularly preferably 100 mol%, of the zirconium compounds, in each case based on the sum of all zirconium compounds, have reacted to give zirconium dioxide.

To produce system II, the precious metal can be impregnated on an inert support, where the support does not consist of the mixed oxide. Preferably, the support does not comprise the mixed oxide or consist of it. For this purpose, every impregnation method known to the person skilled in the art can be used,

such as the application of a precious metal solution to the support.

To produce system III, the precious metal can be impregnated on the mixed oxide as support. For this purpose, every impregnation method known to the person skilled in the art can be used, such as the application of a precious metal solution to the support.

The person skilled in the art can adjust the size of the BET surface area of the mixed oxide by known measures in order to obtain, for example, surface areas of less than 155 m^2/g. The higher the fraction of silicon dioxide in the mixed oxide, the higher the surface area will be. Consequently, at most 14% by weight of silicon dioxide, based on the total weight of the mixed oxide, are present. Furthermore, the calcination temperature influences the surface area: The lower the set temperature, the higher the surface area will be. Consequently, the calcination temperature is not below 300°C, preferably not below 400°C. Moreover, preferably no polymers for enlarging the surface area, as is described for example in EP-A-2108631 (US 2009/0255402), are present. By means of a few experiments, the person skilled in the art is able to undertake an adjustment of the surface area by virtue of the specified parameters.

The mixed oxide can be reshaped into mouldings before or after calcination, preference being given to moulding formation prior to the calcination. The mouldable mass can comprise organic binders (e.g. polymers such as cellulose ethers, polysaccharides, polyethylene oxide), pore formers (e.g. waxes, organic polymers, preferably no organosilicon compounds), inorganic acids such as nitric acid, inorganic bases such as sodium hydroxide solution or mixtures thereof. The acids and/or bases can be used to adjust the rigidity and mouldability of the mixed oxide. Preferably excluded as pore formers for the system III are polyalkylene pyrrolidones such as polyvinylpyrrolidone, polyamines, polyacrylates, polyalcohols, polysiloxanes or mixtures thereof, which encourage the formation of a bimodal pore distribution, as described for example in EP-A-1074301. An example of such a polymer is

poly(vinylpyrrolidone) (PVP).

The invention further provides the use of a catalyst composition K for producing ketones from a compound containing at least one epoxide group. The catalyst composition K comprises at least one precious metal and at least one mixed oxide, where the mixed oxide comprises zirconium dioxide and silicon dioxide and the mass ratio of zirconium dioxide to silicon dioxide in the mixed oxide is 86: 14 to 99.9 to 0.1. The precious metal can be supported on the mixed oxide (system III).

Preferably, a catalyst composition according to the invention or a catalyst composition prepared in accordance with a method according to the invention is used, with system II being preferred.

The invention further provides a process for producing ketones, preferably cyclododecanone, from a compound containing at least one epoxide group, where a catalyst composition K is used. Preferably, a catalyst composition according to the invention or a catalyst composition prepared in accordance with a method according to the invention is used, with system II being preferred.

The process constitutes a heterogeneous catalysis.

The quantitative fraction of precious metal, based on the quantitative amount of the compound containing at least one epoxide group (compound E), can be 0.00001 to 0.1, preferably 0.0001 to 0.01. The quantitative fraction of mixed oxide in the catalyst system, based on the quantitative amount of compound E, can be 0.001 to 100, preferably 0.005 to 5.

The compound E can be aliphatic or cycloaliphatic, with cycloaliphatic compounds being preferred. Preferably, 4 to 20 carbon atoms, preferably 6 to 16 carbon atoms, particularly preferably 8 to 14 carbon atoms, very particularly preferably 10 to 12 carbon atoms and in particular 12 carbon atoms are

comprised.

The compound E can contain one or more epoxide groups, with monoepoxide compounds being preferred.
Furthermore, the compound can be saturated or unsaturated. For example, one or two double bonds can be present.

Preferred compounds E are monoepoxycycloalkanes, monoepoxycycloalkanedienes and monoepoxycycloalkenes, with monoepoxycycloalkanes being particularly preferred. A very particularly preferred compound E is monoepoxycyclododecane.

It has been found that the formation of the corresponding alcohol derivative as by-product depends on the pressure of the hydrogen: As the pressure increases, so too does the alcohol fraction, meaning that the ketone selectivity decreases.

The process according to the invention can be carried out at a hydrogen pressure of from 0 up to 100 bar, with the hydrogen pressure preferably being adjusted to 0 to 5 bar and preferably to 0 to 2.5 bar. The hydrogen pressure is particularly preferably 0 to 0.9 bar, very particularly preferably 0 to 0.5 bar. The process according to the invention can be carried out without hydrogen. However, in order to suppress unsaturated by-products, it is preferred to initially introduce at least a small hydrogen fraction. This can have 0.05 to 0.5 bar, preferably 0.1 to 0.4 bar. Alternatively, a hydrogenation step can be provided following the rearrangement.

The pressure data specified above refers to the partial pressure of hydrogen in the system. Usually, components of the reaction mixture, including of the solvent, air or inert gases such as nitrogen or argon, are further gaseous constituents of the system.

As a result of the low hydrogen pressures, a considerably lower technical

expenditure compared to the prior art is required, especially as regards the suitable apparatus, in order to be able to work with hydrogen. The particular advantage of the invention is that the ketone can be obtained in high yields without the presence of hydrogen.

The temperature during the reaction is preferably adjusted to a range from 100 to 350°C, preferably 150 to 250°C and particularly preferably between 180 and 230°C. The reaction can be carried out with a compound E, which is in the liquid or gaseous state.

The process according to the invention can be carried out in organic solvents, it being preferred to work without solvents and thus to use no organic solvents. Suitable solvents are, for example, alkanes such as n-hexane, n-heptane, n-tetradecane and cyclohexane; ethers such as tetrahydrofuran and dioxane; alkanols such as methanol, ethanol and t-butanol; esters such as ethyl acetate and butyl acetate. The solvents can be used on their own or in mixtures. The solvent is preferably used in an amount which is 20 times or less than, preferably 10 times or less than, the weight of compound E.

The process can be carried out continuously or discontinuously. The purification of the ketone can take place by distillation, crystallization or recrystallization.

In a preferred embodiment of the invention, monoepoxycyclododecane is converted to cyclododecanone without solvents at temperatures of 170 to 250°C, where the catalyst system used is a mixture of palladium on inert support with a palladium fraction of 0.5 to 2% by weight, based on the total weight of the support, and of a mixed oxide from the calcination of a mixture comprising at least zirconium hydroxide and silicon dioxide (system II). During the reaction, at most 0.9 bar of hydrogen, very particularly preferably at most 0.1 bar, are used.

The invention further provides a process for the synthesis of lactams (lactam process according to the invention), in which the aforementioned process

according to the invention for producing ketones is used. The compound E is preferably selected from aliphatic monoepoxycycloalkanes, aliphatic monoepoxycycloalkanedienes and aliphatic monoepoxycycloalkenes, with monoepoxycycloalkanes being preferred.

If the ketone is present in a mixture with the corresponding alcohol derivative, a dehydrogenation of the alcohol to the ketone can take place. The ketone may subsequently be oximated. The Beckmann rearrangement to give the lactam may be carried out as a subsequent step using sulphuric acid or cyanuric chloride. The lactams may be subjected to further processing by polycondensation to give polyamides.

The dehydrogenation, the oximation, the Beckmann rearrangement and the condensation reaction are known to the person skilled in the art.

In a preferred embodiment of the lactam process according to the invention, laurolactam is prepared from monoepoxycyclododecane (or cyclododecane epoxide or 1,2-cyclododecane epoxide).

In the context of the preferred lactam method, monoepoxycyclododecane is obtainable by the following reaction steps: 1,3-butadiene is reacted to give cyclododecatriene by cyclotrimerization. This is followed by a hydrogenation to give the cyclododecene. The cyclododecane epoxide is obtained by subsequent epoxidation. The person skilled in the art in the field of the synthesis of organic compounds can prepare other aliphatic and cycloaliphatic compounds E analogously to the synthesis of monoepoxycyclododecane.

Even in the absence of further information it is assumed that a person skilled in the art can make very extensive use of the above description. The preferred embodiments and examples are therefore to be interpreted merely as descriptive disclosure, and certainly not as disclosure that is in any way limiting.

The present invention is explained in more detail below with reference to examples. Alternative embodiments of the present invention are obtainable analogously.

Examples

The percentages in the case of catalysts give the weight fraction of the precious metal, based on the total weight of the catalyst comprising precious metal and support. The abbreviation "calc." stands for "calcined". The abbreviations for the substances are: CDAN: Cyclododecane; CDEN: Cyclododecene; ECD: Epoxycyclododecane; CDON: Cyclododecanone; CDENON: Cyclododecenone (isomer mixture); CDOL: Cyclododecanol; CDENOL: Cyclododecenol (isomer mixture).

The weight data for the precious metal refer, unless stated otherwise, to the total weight of the support of the precious metal.

The silicon dioxide (Aerosil) used in the examples was obtained via a pyrogenic method.

Preparation of the mixed oxides

Example A (not according to the invention): Preparation of ZrO_2 mouldings

Oxide 1 (100% ZrO_2): 2000 g of zirconium hydroxide powder (XZO 1501/09, MEL Chemicals) were calcined to zirconium dioxide in a muffle furnace at 450°C for 3 h. After cooling, 1000 g of zirconium dioxide powder were mixed with 10 g of cellulose ether (Tylose MH1000 P2 from SE Tylose). 520 g of water were then added, and the mixture was kneaded until an extrudable mass was obtained. The mass was processed and cut using a roller die extruder to give strands with a diameter of 1.6 mm. The green bodies were dried at 110°C for 4 hours and then calcined at 450°C for 2 hours.

The BET surface area of the calcined mouldings was 64 m^2/g. The pore radius distribution was monomodal.

The oxide 1 corresponds to the zirconium dioxide used in table 3, last entry, and table 4, fourth and fifth entry in EP-A-2772478.

Example B: Preparation of mouldings from ZrO_2 and SiO_2 (mixed oxide)

Oxide 2 (95% ZrO_2, 5% SiO_2): 773 g of zirconium dioxide powder (from Example A) were mixed with 40 g of silicon dioxide (Aerosil 200 V, Evonik), and 8 g of Tylose MH1000. Then, 450 g of water were added, and the mixture was kneaded until an extrudable mass was obtained. The mass was processed and cut using a roller die extruder to give strands with a diameter of 1.6 mm. The green bodies were dried at 110°C for 4 hours and then calcined at 450°C for 2 hours.

The pore radius distribution was monomodal.

Oxide 3 (95% ZrO_2, 5% SiO_2): 1000 g of zirconium hydroxide (XZO 1501/09, MEL Chemicals), 40 g of Aerosil 200 V, 20 g of wax (Licowax C Micro Powder PM from Clariant) and 2 g of cellulose ether (Tylose MH1000 P2 from SE Tylose) were introduced in a mixer and dry-mixed. Then, 8.3 g of a 30% strength NaOH solution in 800 g of water were added and the mixture was kneaded until an extrudable mass was obtained. The mass was processed and cut using a roller die extruder to give strands with a diameter of 1.8 mm. The green bodies were dried at 110°C for 4 hours and then calcined at 450°C for 2 hours.

The calcined mouldings comprised ZrO_2 and SiO_2 in a mass ratio of 95:5. The calcined mouldings had an average diameter of 1.16 mm and a BET surface area of 150 m^2/g.

Further oxides (4 to 9) were prepared under analogous conditions. The following were varied: the amount of zirconium hydroxide, silicon dioxide, and also type and amount of the zirconium compounds B and inorganic acids and/or bases. As pulverulent shaping auxiliary, 20 g of Licowax and 2 g of Tylose MH1000 P2 were always added. The precise conditions are given in the table below.

In the oxides 10 and 11, ammonium zirconium carbonate (Bacote 20, oxide 10)

or zirconyl nitrate (oxide 11) were used as zirconium compound B.

Example C (not according to the invention): preparation of ZrO_2-doped SiO_2

Oxide 12 (15% ZrO_2, 85% SiO_2): 85g of SiO_2 support (Aerolyst® 3041, Evonik) were impregnated with 85 ml of a 5.5% by weight NaOH solution and dried at 110°C for 4h. In parallel to this, 40g of $ZrOCl_2$. $8H_2O$ were dissolved in water and the solution was diluted to 85 ml. The dried support was impregnated with the zirconyl chloride solution, dried overnight at 110°C and then calcined at 450°C for 2 hours.

Oxide 13 (15% ZrO_2, 85% SiO_2): 50g of a 30% zirconium acetate solution ($Zr(OA_c)$ was diluted to 85 ml. 85g of SiO_2 support (Aerolyst® 3041, Evonik) was impregnated with the zirconyl chloride solution, dried over night at 110°C and then calcined at 450°C for 2 hours.

The pore radius distributions of all of the supports in examples A to C were monomodal.

Table 1. Overview of the prepared mixed oxides

Oxide	Zr Precursor	SiO_2	Other	ZrO_2:SiO_2 (mass ratio)	BET (m^2/g)
3	1000 g $Zr(OH)_4$	40 g Aerosil 200V	8.3 g of a 30% strength NaOH solution in 800 g of H_2O	95:5	150
4	1000 g $Zr(OH)_4$	8 g Aerosil 200V	65.4 g of a 65% strength HNO_3 solution in 530 g of H_2O	99:1	78
5	1000 g $Zr(OH)_4$	24 g Aerosil 200V	66 g of a 65% strength HNO_3 solution in 550 g of H_2O	97:3	79
6	1000 g $Zr(OH)_4$	40 g Aerosil 200V	84 g of a 65% strength HNO_3 solution in 541 g of H_2O	95:5	86
7	1000 g $Zr(OH)_4$	85.5 g Aerosil 200V	84 g of a 65% strength HNO_3 solution in 565 g of H_2O	90:10	109
8*	894 g $Zr(OH)_4$	122 g Aerosil 200V	7.45 g of a 30% strength NaOH solution in 830 g of H_2O	85:15	213
9*	1000 g $Zr(OH)_4$	142 g tetraethyl orthosilicate	400 g water	95:5	---
10	1000 g $Zr(OH)_4$	40 g Aerosil 200 V	8.3 g of a 30% strength NaOH solution in 700 g of H_2O, 118 g Bacote 20 (MEL Chemicals)	95:5	131
11	1000 g $Zr(OH)_4$	40 g Aerosil 200 V	90 g of a 65% strength HNO_3 solution in 450 g of H_2O, 118 g zirconyl nitrate (MEL Chemicals)	95:5	113
12*	40 g $ZrOCl_2$·	85 g silica support	85 ml of a 5.5% by weight NaOH solution	15:85	---

	8 H_2O				
13*	50 g $Zr(OAc)_4$ (30% strength)	85 g silica support	---	15:85	---

** not according to the invention*

Catalyst compositions

Example D: Composition of mixed oxide and Pd-impregnated silicon dioxide (catalyst system II)

2000 g of silicon dioxide mouldings (Aerolyst® 3041, Evonik) were introduced into a rotating glass drum and heated to 110°C. In parallel, 100 g of a 10% strength Pd(II) nitrate solution were weighed and diluted to 1910 g by adding water. The solution was then sprayed onto the SiO_2 support. A thin precious metal shell was formed. The impregnated mouldings were then calcined for 10 hours in a reducing atmosphere (0.4% by volume hydrogen in the nitrogen) at 200°C. The weight fraction of Pd with regard to the SiO_2 support was 0.5%. These Pd/SiO_2 mouldings were compounded with the various oxides 1 to 13 from Examples A, B, C.

Catalyst compositions:

- Composition 1*: Oxide 1 (50% by weight) and Pd/SiO_2 (50% by weight) and Pd/SiO_2(50% by weight); this composition comprises the same constitutents as the catalyst compositions used in table 3, last entry and table 4, fourth and fifth entry in EP-A-2772478.
- Composition 2: Oxide 2 (50% by weight) and Pd/SiO_2 (50% by weight)
- Composition 3: Oxide 3 (50% by weight) and Pd/SiO_2 (50% by weight)
- Composition 4: Oxide 4 (50% by weight) and Pd/SiO_2 (50% by weight)
- Composition 5: Oxide 5 (50% by weight) and Pd/SiO_2 (50% by weight)
- Composition 6: Oxide 6 (50% by weight) and Pd/SiO_2 (50% by weight)
- Composition 7: Oxide 7 (50% by weight) and Pd/SiO_2 (50% by weight)
- Composition 8*: Oxide 8 (50% by weight) and Pd/SiO_2 (50% by weight)
- Composition 9*: Oxide 9 (50% by weight) and Pd/SiO_2 (50% by weight)
- Composition 10: Oxide 10 (23% by weight) and Pd/SiO_2 (77% by weight)
- Composition 11: Oxide 11 (23% by weight) and Pd/SiO_2 (77% by weight)
- Composition 12: Oxide 3 (9% by weight) and Pd/SiO_2 (91% by weight)
- Composition 13: Oxide 3 (23% by weight) and Pd/SiO_2 (77% by weight)

- Composition 14 : Oxide 3 (33% by weight) and Pd/SiO_2 (67% by weight)
- Composition 15 : Oxide 6 (20% by weight) and Pd/SiO_2 (80% by weight)
- Composition 16*: TiO_2-SiO_2 mixture (calcined) *VP TiO2 545 S* from pyrogenic process of Evonik Industries (9% by weight) and Pd/SiO_2 (91% by weight)
- Composition 17*: TiO_2-SiO_2 mixture (calcined) *VP TiO2 590 S* from pyrogenic process of Evonik Industries (9% by weight) and Pd/SiO_2 (91% by weight)
- Composition 18*: SiO_2 Aerosil® 200V (50% by weight) and Pd/SiO_2 (50% by weight)
- Composition 19*: oxide 12 (50% by weight) and Pd/SiO_2 (50% by weight)
- Composition 20*: oxide 13 (50% by weight) and Pd/SiO_2 (50% by weight)
- Composition 21*: oxide 1 (33.3% by weight) and Pd/SiO_2 (67.7% by weight); this composition corresponds to the catalyst composition used in table 3, last entry, in EP-A-2772478
- Composition 22*: oxide 1 (9% by weight) and Pd/SiO_2 (91% by weight); this composition comprises the same constituents as the catalyst compositions used in table 3, last entry, and table 4, fourth and fifth entry, in EP-A-2772478

** not according to the invention*

Compositions 1, 21 and 22 comprise no mixed oxide for the purposes of the invention; they are physical mixtures of zirconium dioxide and silicon dioxide (SiO_2 as support).

Example E: Pd supported on mixed oxide (catalyst system III)

75 g of oxide mouldings according to Example C were weighed in a polybag. In parallel, 3.75 g of a 10% strength Pd(II) nitrate solution were weighed and diluted to 45 ml by adding water. The diluted solution was poured onto the mouldings in the polybag, and the bag was always shaken again until the liquid was distributed homogeneously on the mouldings. The impregnated mouldings

were dried at 110°C for 2.5 hours, and then calcined for 10 hours in a reducing atmosphere (0.4% by volume hydrogen in the nitrogen) at 200°C. The weight fraction of Pd in the catalyst, based on the total weight of the mixed oxide, was 0.5%.

Catalyst compositions:

- Composition 23*: Oxide 1 supported with 0.5% by weight Pd
- Composition 24*: Oxide 1 supported with 0.5% by weight Pd (95% by weight), after the impregnation and calcination mixed with SiO_2 Aerosil® 200V (5% by weight). Here, a physical mixture of ZrO_2 and SiO_2 is present, not a mixed oxide.
- Composition 25: Oxide 3 with 0.5% by weight Pd

* not according to the invention

Catalyst test

Gas chromatography (GC): Gas chromatographic investigations were carried out using a GC-2010 (Shimadzu) chromatograph, fitted with autosampler, flame ionization detector (FID), and GC capillary column Supelcowax® (60 m × 0.32 mm × 0.25 µm, Supelco). Measurements were carried out in the split mode (Split rate 1: 66) with helium as carrier gas (flow rate 0.89 ml/min, linear carrier gas rate 17.9 cm/sec). Temperature programme for GC oven: Start temperature 150°C; heat to 180°C at 5°C/min, hold for 10 min; heat to 200°C at 5°C/min, hold for 10 min. Detector and injector temperatures were 340 and 220°C.

Example 1: Comparison of different oxides (catalyst system II)

The reaction was carried out in a 500 ml round-bottomed flask with mechanical stirring. The heating of the reactor was carried out with an electric aluminium heating block and the internal temperature was controlled using a thermosensor. The flask was filled with 50 ml of 1,2-cyclododecane epoxide, 20 g of catalyst compositions from Example D. The catalyst bed lay at the bottom of the flask and the liquid reaction mixture was stirred above the bed. The flask was then rendered inert with nitrogen and heated to an internal

temperature of 215°C. The temperature was held for 1.5 hours.

Table 2. Composition (area %, GC) of the reaction mixture (after 1.5 h)

Catalyst composition	Conversion (%)	Selectivity (%)				
		CDAN	CDEN	CDON + CDENON	CDOL	CDENOL
*1** (physical mixture)	28	0	0	74	6	18
2 (ZrO_2-SiO_2 95/5)	64	0.6	0	79	6	14
4 (ZrO_2-SiO_2 99/1)	55	0	0	90	5	5
5 (ZrO_2-SiO_2 97/3)	71	0	0.6	81	9	10
3 (ZrO_2-SiO_2 95/5)	97	0.4	3	79	6	11
6 (ZrO_2-SiO_2 95/5)	80	0.1	1.5	79	7	10
7 (ZrO_2-SiO_2 90/10)	97	0.1	5	69	9	13
*8** (ZrO_2-SiO_2 85/15, BET>200)	95	0	10	66	6	17
*9** (Organo-Si source)	77	0	2	16	1	72
*16** (TiO_2-SiO_2 95/5)	51	1	1	3	0.5	60
*17** (TiO_2-SiO_2 95/5)	60	0.9	2	7	0.7	63
*18** (SiO_2)	< 1	Not relevant				
*19** (ZrO_2-SiO_2 15/85)	86	0.3	9	70	9	11
*20** (ZrO_2-SiO_2 15/85)	>99	<1% CDON formed, (see table 4)				

**not according to the invention*

Table 2 shows the selectivities for CDO and CDENON in summary since these are technically relevant. The background is that CDENON is usually reacted by the addition of hydrogen in CDON. In this regard, CDENON is not a byproduct. Nevertheless, for the sake of completeness, CDON and CDENON are differentiated in table 3 below.

Table 3. Composition (area %, GC) of the reaction mixture (after 1.5h)

according to table 2; division of the mixture CDON + CDENON

Catalyst composition	Conversion (%)	Selectivity(%)		
		CDON	CDENON	CDON + CDENON
*1** (physical mixture)	28	68	6	74
2 (ZrO_2-SiO_2 95/5)	64	72	7	79
4 (ZrO_2-SiO_2 99/1)	55	84	6	90
5 (ZrO_2-SiO_2 97/3)	71	74	7	81
3 (ZrO_2-SiO_2 95/5)	97	69	10	79
6 (ZrO_2-SiO_2 95/5)	80	69	10	79
7 (ZrO_2-SiO_2 90/10)	86	54	15	69
*8** (ZrO_2-SiO_2 85/15, BET>200)	95	52	14	66
*9** (Organo-Si source)	77	12	4	16
*16** (TiO_2-SiO_2 95/5)	51	0	3	3
*17** (TiO_2-SiO_2 95/5)	60	0	7	7
*18** (SiO_2)	< 1	Not relevant		
*19** (ZrO_2-SiO_2 15/85)	86	53	17	70
*20** (ZrO_2-SiO_2 15/85)	>99	< 1 % CDON formed (see table 4)		

**not according to the invention*

With the same reaction time, the conversion with composition 1 was considerably lower than with compositions 2 to 7. It was found that the mixed oxides ZrO_2-SiO_2 have a much higher catalytic activity than pure ZrO_2 from the prior art for a similar selectivity to the ketone. The activity increased with the fraction of SiO_2 in the mixed oxide.

With composition 8, 10% of the by-product CDEN were obtained, meaning that this catalyst cannot be used cost-effectively on account of the low selectivity. An SiO_2 fraction of > 15% by weight in the mixed oxide and a BET surface area > 200 m^2/g are not preferred for this reason.

Compositions 9 (organosilicon source) and 16 and 17 (chemical mixture of

TiO_2 and SiO_2) exhibit a very low selectivity to CDON.

Composition 18 has no catalytic activity. This experiment confirms that ZrO_2 in the catalyst system forms an obligatory necessary constituent.

Composition 19 (zirconium dioxide-doped silicon oxides) exhibits relatively high conversions and high selectivities. However, the data presented in tables 2 and 3 do not take into consideration the formation of high boilers (oligomers and polymers) which are formed during the reaction. The values for the high boilers are taken into consideration in table 4 below.

Table 4. Composition (% by weight, calculated with GC factors) of some reaction mixtures after 5h taking into consideration the high boilers

Catalyst composition	CDAN + CDEN	Epoxide	CDON	CDEN-ON	CDOL	CDEN-OL	High boilers (oligomers/ polymers)
*1** (physical mixture)	0.3	42	51	3	2.6	1.7	0.3
3 *(ZrO_2-SiO_2 95/5)*	2.7	0	79	9	5	1.4	2.6
*19** *(ZrO_2-SiO_2 15/85)*	9	0	54	12	5	2.4	17
*20** *(ZrO_2-SiO_2 15/85)*	1	0.4	0.5	9	0.25	4	85

**not according to the invention*

With compositions 19 and 20, in each case zirconium-doped silicon dioxide, fractions of 17% and 85%, respectively, of high boilers are obtained. The composition according to the invention comprising the mixed oxide, by contrast, has only 2.6% high boilers as byproduct. Consequently, a zirconium dioxide-doped or coated silicon dioxide is not suitable as catalyst system.

Example 2: Comparison of different oxides (catalyst system II) – progress with time

The aforementioned reaction in example 1 was continued for compositions 1 and 3 up to a reaction time of 5h. Samples were taken regularly and the conversion of the starting material 1, 2-cyclododecane epoxide was

determined. Moreover, a further experiment with 30g of composition 21 was carried out.

Table 5. Conversion of the starting material 1,2-cyclodo decane epoxide over a period of 5h (area %, GC)

Catalyst composition	Symbol in Fig. 1	Conversion of starting material				
		0 h	0.5 h	1.5 h	3.0 h	5.0 h
*1** *(physical mixture)*	Diamond	0 %	5 %	28 %	46 %	58 %
3 *(ZrO_2-SiO_2 95/5)*	Square	0 %	67 %	97 %	100 %	100 %
21* *(physical mixture)*	Triangle	0 %	40 %	80 %	94 %	100 %

**not according to the invention*

Composition 3 according to the invention leads, after just 1.5h, to a virtually complete conversion of the starting material used, which reaches 100% after 3h. Mixture 1 does not achieve this value even after a reaction time of 5h. Although mixture 21 of the prior art (EP-A-2772478, table 3, last entry) likewise exhibits a complete conversion, this is present only after a significantly longer reaction time and is achieved with a larger amount of catalyst composition.

The progress of the composition is shown graphically in Figure 1. Here, the conversion U of 1,2-cyclododecane epoxide (in%) was plotted against the reaction time t in hours.

Example 3: Precious metal supported on the mixed oxide (catalyst system III)

The reaction was carried out in a 500 ml round-bottomed flask with mechanical stirring. The heating of the reactor was carried out with an electric aluminium heating block and the internal temperature was controlled using a thermosensor. The flask was filled with 50 ml of 1,2-cyclododecane epoxide and the catalyst composition (Example E). The catalyst bed lay at the bottom of the flask and the liquid reaction mixture was stirred above the bed. The flask was then rendered inert with nitrogen and heated to an internal temperature of 215°C. The temperature was held for 1.5 hours.

Table 6. Composition (area %, GC) of the reaction mixture (after 1.5 h)

Catalyst composition	Amount (g)	Conversion (%)	Selectivity (%)				
			CDAN	CDEN	CDON	CDOL	CDENOL
*23** *(ZrO_2)*	10	35	0	0	94	4	0
25 *(ZrO_2-SiO_2 95/5)*	10	98	0.3	1.1	79	8	3
*23** *(ZrO_2)*	20	80	1	0	96	3	0
*24** *(physical mixture)*	20	69	1	0	97	2	0
25 *(ZrO_2-SiO_2 95/5)*	20	>99	0.5	1.4	87	5	2

*not according to the invention

Example 3 has demonstrated that ZrO_2-SiO_2 mixed oxides of catalyst system III have a catalytic activity. This turned out to be considerably higher for the mixed oxide (composition 25) than for catalysts without SiO_2 (composition 23) or catalysts comprising a physical mixture of ZrO_2 and SiO_2 (composition 24).

Example 4: Optimized reaction conditions (catalyst system II)

The reaction was carried out in a 500 ml round-bottomed flask with mechanical stirring. The heating of the reactor was carried out with an electric aluminium heating block and the internal temperature was controlled using a thermosensor. The flask was filled with 50 ml of 1,2-cyclododecane epoxide and 13 g of the catalyst composition. The catalyst bed lay at the bottom of the flask and the liquid reaction mixture was stirred above the bed. The flask was then rendered inert with nitrogen and heated to an internal temperature of 215°C. The temperature was held for 6 hours.

The weight ratio of ZrO_2 to SiO_2 was 95:5 for all three catalyst compositions. Similarly, the weight ratio of oxide to Pd on an inert support was identical (23:67). The oxides were prepared either from zirconium hydroxide or from zirconium hydroxide and a compound B.

Table 7. Composition (area %, GC) of the reaction mixture (after 6 h)

Catalyst composition	Conversion (%)	Selectivity (%)				
		CDAN	CDEN	CDON + CDENON	CDOL	CDENOL
10 (Ammonium zirconium carbonate)	98	1	0.4	87	5	4
11 (Zirconyl nitrate)	67	0.1	1.3	88	6	4
13 (no compound B)	98	0.1	1.2	91	4	1.3

A second zirconium compound B, in addition to the zirconium hydroxide A, was added in the preparation of the mixed oxides 10 and 11. Composition 13 was prepared with zirconium hydroxide A as single Zr source. The catalyst compositions are thus suitable for the rearrangement of the epoxide to the ketone irrespective of the composition of the zirconium compound.

Analogously to table 7, the fractions of CDON and CDENON are listed individually in table 8.

Table 8. Composition (area %, GC) of the reaction mixture (after 1.5h) according to table 7; division of the mixture CDON + CDENON

Catalyst composition	Conversion (%)	Selectivity (%)		
		CDON	CDENON	CDON + CDENON
10 (ammonium zirconium carbonate)	98	79	8	87
11 (zirconyl nitrate)	67	79	9	88
13 (no compound B)	98	84	7	91

Example 5: Optimized reaction conditions (catalyst system II)

The reaction was carried out in a 500 ml round-bottomed flask with mechanical stirring. The heating of the reactor was carried out with an electric aluminium

heating block and the internal temperature was controlled using a thermosensor. The flask was filled with 50 ml of 1,2-cyclododecane epoxide, and 10 g of 0.5% by weight palladium on silicon dioxide as moulding and the mixed oxide of the catalyst system (moulding). The catalyst bed lay at the bottom of the flask and the liquid reaction mixture was stirred above the bed. The flask was then rendered inert with nitrogen and heated to an internal temperature of 180 to 215°C. The temperature was held over the stated time.

Table 9. Composition (area %, GC) of the reaction mixture

Catalyst composition	Mixed oxide	Temp (°C)	Time (h)	Conversion (%)	Selectivity (%)			
					CDAN	CDEN	CDON + CDENON	CDOL
1*	*10 g oxide 1*	215	5	58	0	0.2	92	4
22*	*1 g oxide 1*	215	5	13	0	0	95	4
12	*1 g oxide 3*	215	5	50	0.4	1	92	3
1*	*10 g oxide 1*	215	24	98	0	0	97	2
22*	*1 g oxide 1*	215	24	38	0	0	96	3
12	*1 g oxide 3*	215	24	98	0	1.5	94	4
13	*3 g oxide 3*	200	24	99	0.2	0.5	95	3
1*	*10 g oxide 1*	180	24	19	0	0	94	3
3	*10 g oxide 3*	180	24	>99	0	0.7	93	5

*not according to the invention

Table 10. Composition (area %, GC) of the reaction mixture according to table 9; division of the mixture CDON + CDENON

Catalyst composition	Mixed oxide	Temp (°C)	Time (h)	Conversion (%)	Selectivity (%)		
					CDON	CDENON	CDON + CDENON
1*	*10 g oxide 1*	215	5	58	87	5	92
22*	*1 g oxide 1*	215	5	13	94	1	95
12	*1 g oxide 3*	215	5	50	75	17	92
1*	*10 g oxide 1*	215	24	98	95	2	97
22*	*1 g oxide 1*	215	24	38	95	1	96
12	*1 g oxide 3*	215	24	98	87	7	94
13	*3 g oxide 3*	200	24	99	90	5	95
1*	*10 g oxide 1*	180	24	19	92	2	94
3	*10 g oxide 3*	180	24	>99	86	7	93

**not according to the invention*

A comparison of composition 12 according to the invention (ZrO_2-SiO_2 mixed oxide) with compositions 1 and 22 not according to the invention (prior art) over a reaction time of 5 h at 215°C demonstrates that less than 1/10 of ZrO_2 is required for the same catalytic activity. With the same amount of zirconium dioxide, composition 12 according to the invention exhibits a much higher catalytic activity than composition 22 (prior art).

The 24-hour experiment demonstrates that for a similarly high conversion with a simultaneously similarly high selectivity, compared to composition 1, less catalyst (compositions 12, 13) or a lower temperature are required (compositions 13, 3).

Example 6: Reaction of epoxide

The reaction was carried out in a 500 ml round-bottomed flask with mechanical stirring. The heating of the reactor was carried out with an electric aluminium heating block and the internal temperature was controlled using a thermosensor. The flask was filled with 50 ml of 1,2-cyclododecane epoxide, 10 g of 0.5% by weight of palladium on silicon dioxide as moulding and 5 g of oxide 3 (corresponds to 15 g of composition 14). The catalyst bed lay at the bottom of the flask and the liquid reaction mixture was stirred above the bed. A mixture of hydrogen and nitrogen was introduced during the reaction (1 bar with 90% by volume H_2 and 10% by volume N_2). The flask was then heated to an internal temperature of 215°C. The temperature was held for 5 hours. At the end of the experiment, a mixture of CDON (87.2%), CDOL (8.4%), CDAN (2%) and CDENOL (1%) was obtained.

Example 7: Fixed-bed method

The reaction was carried out in a fixed-bed arrangement. The arrangement consisted of two fixed-bed reactors in series (approx. 200 ml per reactor) and a steel storage container (1 l). The lower fixed-bed reactor was filled with 50 g of oxide 6 and the upper fixed-bed reactor was filled with 200 g of 0.5% Pd/SiO_2 from Example D. This composition corresponds to 250 g of catalyst composition 15. The container was filled with 1500 g of 1,2-cyclododecane epoxide. The liquid was pumped in a cycle from the storage container from bottom to top through the catalyst bed back to the storage container using a circulating pump (10 l/h). The reactors were heated to 205°C in the reaction mixture using electrical heating. The reaction mixture was passed through the fixed-bed reactors and the container with nitrogen. After a reaction of 30 h, a conversion of 78% with a selectivity of approx. 93% CDON was achieved.

Table 11. Composition (area %, GC) of the reaction mixture

Temp (°C)	Time (h)	Conversion (%)	Selectivity (%)					
			CDAN	CDEN	CDON	CDENON	CDOL	CDENOL

205	30	78	0.4	1	93	0.9	4	0.4

The reaction can be carried out with the catalyst systems according to the invention in fixed-bed reactors. This experiment also shows that both components of catalyst system II (ZrO_2-SiO_2 mixed oxide as moulding and Pd/SiO_2 moulding) can be used in spatially separate reactors without an adverse effect on the activity and selectivity.

Claims

1. Catalyst composition comprising at least one metal and at least one mixed oxide, wherein the metal is selected from ruthenium, rhodium, palladium, osmium, iridium, platinum and mixtures thereof, wherein the mixed oxide comprises zirconium dioxide and silicon dioxide, wherein the metal is supported and the support does not consist of the mixed oxide, and wherein the mass ratio of zirconium dioxide to silicon dioxide in the mixed oxide is 86: 14 to 99.9: 0.1.

2. Catalyst composition according to Claim 1, wherein the support does not comprise the mixed oxide.

3. Catalyst composition according to either of the preceding claims, wherein the support of the metal is selected from silicon dioxide, aluminium oxide or mixtures thereof.

4. Process for producing the catalyst composition according to one of the preceding claims, wherein for the preparation of the mixed oxide,

   a) a mouldable mass is prepared which at least comprises
      i. a zirconium compound,
      ii. silicon dioxide as solid, preferably produced by means of pyrogenic methods, and
      iii. water, and
   b) the mouldable mass is calcined at a temperature of from 300 to 500°C.

5. Process according to Claim 4, wherein the metal is

impregnated on an inert support to produce the catalyst system and wherein the metal is selected from ruthenium, rhodium, palladium, osmium, iridium, platinum and mixtures thereof.

6. Process for producing a catalyst composition, wherein the catalyst composition comprises at least one metal and at least one mixed oxide, wherein the metal is selected from ruthenium, rhodium, palladium, osmium, iridium, platinum and mixtures thereof, wherein the mixed oxide comprises zirconium dioxide and silicon dioxide, the specific surface area of the mixed oxide, measured according to BET methods, is 5 – 155 m^2/g, the metal is supported on the mixed oxide, the mixed oxide has a monomodal pore radius distribution, wherein the mass ratio of zirconium dioxide to silicon dioxide in the mixed oxide is 86: 14 to 99.9: 0.1, and wherein for the preparation of the mixed oxide,

   a) a mouldable mass is prepared which at least comprises
      i. a zirconium compound,
      ii. silicon dioxide as solid having a particle size d_{50} (laser diffraction) of at least 100 nm, preferably produced by means of pyrogenic methods, and
      iii. water, and
   b) the mouldable mass is calcined at a temperature of from 300 to 500°C.

7. Process according to Claim 6, wherein the metal is impregnated on the mixed oxide as support.

8. Process according to one of Claims 4 to 7, wherein the particle size d_{50} (laser diffraction) of the silicon dioxide is 100 nm to 500 µm.

9. Process according to one of Claims 4 to 8, wherein the zirconium compound is selected from zirconium dioxide, zirconium hydroxide, zirconium acetate, zirconium nitrate, zirconium oxychloride, ammonium zirconium carbonate or mixtures thereof, preferably zirconium dioxide, zirconium hydroxide or mixtures thereof.

10. Process according to Claim 9, wherein the zirconium compound is a mixture of A and B, where

A is selected from zirconium dioxide, zirconium hydroxide and mixtures thereof and

B is selected from zirconium acetate, zirconium nitrate, zirconium oxychloride, ammonium zirconium carbonate and mixtures thereof.

11. Process according to one of Claims 4 to 10, wherein the mouldable mass is reshaped to give mouldings prior to the calcination.

12. Process for producing ketones, preferably cyclododecanone, from a compound containing at least one epoxide group, wherein a catalyst composition is used which comprises at least one metal and at least one mixed oxide, wherein the metal is selected from ruthenium, rhodium, palladium, osmium, iridium, platinum and mixtures thereof and wherein the mixed oxide comprises zirconium dioxide and silicon dioxide, the metal is supported on a support, wherein the mass ratio of zirconium dioxide to silicon dioxide in the mixed oxide is 86: 14 to 99.9: 0.1, and wherein the support is the mixed oxide or the support does not consist of the mixed oxide.

13. Process for the synthesis of lactams, in which the process for producing ketones according to Claim 12 is used.