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Catalyst and process for the hydrogenation of carbonyl compounds

The present invention relates to a process for the hydrogenation of organic compounds containing at least one carbonyl group using a catalyst which comprises copper oxide, aluminum oxide and iron oxide and is formed by addition of iron oxide so as to produce a catalyst having a high selectivity and at the same time a high stability. In its production, copper powder, copper flakes or cement can additionally be added. The present invention likewise relates to the catalyst itself and quite generally to the use of lanthanum oxide in the production of catalysts having high selectivity combined with high stability.

The catalytic hydrogenation of carbonyl compounds such as carboxylic acids or carboxylic esters occupies an important position in the production lines of the basic chemicals industry.

In industrial processes, the catalytic hydrogenation of carbonyl compounds such as carboxylic esters is carried out virtually exclusively in fixed-bed reactors. Fixed-bed catalysts used are, apart from catalysts of the Raney type, especially support catalysts, for example copper, nickel or noble metal catalysts.

US 3,923,694 describes, for example, a catalyst of the copper oxide/zinc oxide/aluminum oxide type. The disadvantage of this catalyst is that it has insufficient mechanical stability during the reaction and therefore disintegrates relatively quickly. This results in a drop in activity and the building-up of a differential pressure over the reactor due to the disintegrating catalyst bodies. As a consequence, the plant has to be shut down prematurely.

DE 198 09 418.3 describes a process for the catalytic hydrogenation of a carbonyl compound in the presence of a catalyst comprising a support, which comprises predominantly titanium dioxide, and, as active component, copper or a mixture of copper with at least one metal selected from the group consisting of zinc, aluminum, cerium, noble metals and metals of transition group VIII, with the surface area of copper being not more than $10 \text{ m}^2/\text{g}$. Preferred support materials are mixtures of titanium dioxide with aluminum oxide or zirconium oxide or

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aluminum oxide and zirconium oxide. In a preferred embodiment, the catalyst material is shaped with addition of metallic copper powder or copper flakes.

DE-A 195 05 347 describes, quite generally, a process of catalyst pellets having a high mechanical strength, with a metal powder or a powder of a metal alloy being added to the material to be pelletized. Aluminum powder or copper powder or copper flakes, inter alia, is added as metal powder. However, in the case of a copper oxide/zinc oxide/aluminum oxide catalyst, the addition of aluminum powder gives a shaped body which has poorer lateral compressive strength than a shaped body produced without addition of aluminum powder, and, when used as catalyst, the shaped body of the invention displayed a poorer conversion activity than did catalysts produced without addition of aluminum powder. The document likewise discloses a hydrogenation catalyst comprising NiO, ZrO₂, MoO₃ and CuO, in which Cu powder, inter alia, was mixed during its production. However, this document gives no information on the selectivity or the activity.

DE 256 515 describes a process for preparing alcohols from synthesis gas using catalysts based on Cu/Al/Zn which are obtained by comilling and pelletization with metallic copper powder or copper flakes. The process described is mainly directed at the preparation of mixtures of C₁-C₅-alcohols, and the process is carried out in a reactor whose upper third contains a catalyst having a relatively high proportion of copper powder or copper flakes and whose lower third contains a catalyst having a lower proportion of copper powder or copper flakes.

It is an object of the present invention to provide a process and catalyst which overcome the disadvantages of the prior art and to provide processes for the catalytic hydrogenation of carbonyl compounds and to provide catalysts which have both a high mechanical stability and a high hydrogenation activity and selectivity.

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We have found that this object is achieved by simultaneous precipitation of a copper compound, an aluminum compound and an iron compound and subsequent drying, calcination, tableting and by addition of metallic copper powder, copper flakes or cement powder or graphite or a mixture, giving a catalyst

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which, due to the addition of an iron compound, displays high activities and selectivities and has a high stability of the shaped body used as catalyst.

5 The present invention accordingly provides a process for the hydrogenation of an organic compound containing at least one carbonyl group, which comprises bringing the organic compound in the presence of hydrogen into contact with a shaped body which can be produced by a process in which

- 10 (i) an oxidic material comprising copper oxide, aluminum oxide and iron oxide is made available,
- (ii) pulverulent metallic copper, copper flakes, pulverulent cement or graphite or a mixture thereof can be added to the oxidic material, and
- 15 (iii) the mixture resulting from (ii) is shaped to form a shaped body.

Iron oxide is understood to mean Fe(III) oxide.

20 In preferred embodiments, the shaped bodies of the present invention are used as uniform-composition catalysts, impregnated catalysts, coated catalysts and precipitated catalysts.

25 The catalyst used in the process of the invention is distinguished by the active component copper, the component aluminum and the component iron preferably being precipitated simultaneously or in succession by means of a sodium carbonate solution and subsequently dried, calcined, tableted and calcined again.

In particular the following precipitation method is useful:

- 30 A) A copper salt solution, an aluminum salt solution and a solution of an iron salt or a solution comprising a copper salt, an aluminum salt and an iron salt is/are precipitated in parallel or in succession by means of a sodium carbonate solution. The precipitated material is subsequently dried and, if appropriate, calcined.

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B) Precipitation of a copper salt solution and a solution of an iron salt or a solution comprising a copper salt and at least one salt of iron onto a prefabricated aluminum oxide support. In a particularly preferred embodiment, this is present as powder in an aqueous suspension.
5 However, the support material can also be in the form of spheres, extrudates, crushed material or pellets.

B1) In an embodiment (I), a copper salt solution and a solution of an iron salt or a solution comprising a copper salt and a salt of iron is precipitated,
10 preferably by means of sodium carbonate solution. An aqueous suspension of the support material aluminum oxide is used as initial charge.

Precipitates resulting from A) or B) are filtered and preferably washed free of alkali
15 in a customary manner, as is described, for example, in DE 198 09 418.3.

Both the end products from A) and those from B) are dried at from 50 to 150°C, preferably at 120°C and subsequently calcined if appropriate, preferably for 2 hours at generally from 200 to 600°C, in particular from 300 to 500°C.

20 As starting materials for A) and/or B), it is in principle known to use all Cu(I) and/or Cu(II) salts which are soluble in the solvents used for application to the support, for example nitrates, carbonates, acetates, oxalates or ammonium complexes, analogous aluminum salts and iron salts. For methods A) and B), particular
25 preference is given to using copper nitrate.

In the process of the present invention, the above-described dried and if appropriate calcined powder is preferably converted into pellets, rings, annular pellets, extrudates, honeycombs or similar shaped bodies. All suitable methods
30 known from the prior art are conceivable for this purpose.

The composition of the oxidic material is generally such that the proportion of copper oxide is in the range from 40 to 90% by weight, the proportion of oxides of the iron oxide is in the range from 0 to 50% by weight and the proportion of
35 aluminum oxide is up to 50% by weight, in each case based on the total weight of

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the abovementioned oxidic constituents, with these three oxides together making up at least 80% by weight of the oxidic material after calcination and cement not being included as part of the oxidic material in the above sense.

5 In a preferred embodiment, the present invention accordingly provides a process as described above in which the oxidic material comprises

- 10 (a) copper oxide in a proportion in the range $50 \leq x \leq 80\%$ by weight, preferably $55 \leq x \leq 75\%$ by weight,
- (b) aluminum oxide in a proportion in the range $15 \leq y \leq 35\%$ by weight, preferably $20 \leq y \leq 30\%$ by weight, and
- 15 (c) iron oxide in a proportion in the range $1 \leq z \leq 30\%$ by weight, preferably $2 \leq z \leq 25\%$ by weight,

in each case based on the total weight of the oxidic material after calcination, where $80 \leq x + y + z \leq 100$, in particular $95 \leq x + y + z \leq 100$.

20 The process of the present invention and the catalysts of the present invention are distinguished by the fact that the addition of iron in the precipitation leads to a high stability of the shaped body used as catalyst.

(In general, the amount of pulverulent copper, copper flakes or pulverulent cement
25 or graphite or a mixture thereof is contained to the oxidic material is in the range from 1 to 40% by weight, preferably in the range from 2 to 20% by weight and particularly preferably in the range from 3 to 10% by weight, in each case based on the total weight of the oxidic material.

30 As cement, preference is given to using an alumina cement. The alumina cement particularly preferably consists essentially of aluminum oxide and calcium oxide, in particular it comprises from about 75 to 85% by weight of aluminum oxide and from about 15 to 25% by weight of calcium oxide. It is also possible to use a cement based on magnesium oxide/aluminum oxide, calcium oxide/silicon oxide
35 and calcium oxide/aluminum oxide/iron oxide.

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In particular, the oxidic material may further comprise a proportion of not more than 10% by weight, preferably not more than 5% by weight, based on the total weight of the oxidic material, of at least one additional component selected from the group consisting of the elements Re, Fe, Ru, Co, Rh, Ir, Ni, Pd and Pt.

In a further preferred embodiment of the process of the invention, graphite is added in addition to the copper powder, the copper flakes or the cement powder or the mixture thereof to the oxidic material prior to shaping to form the shaped body. Preference is given to adding such an amount of graphite that shaping to form a shaped body can be carried out more readily. In a preferred embodiment, from 0.5 to 5% by weight of graphite, based on the total weight of the oxidic material, is added. Here, it is immaterial whether the graphite is added to the oxidic material before or after or simultaneously with the copper powder, the copper flakes or the cement powder or the mixture thereof.

The present invention accordingly also provides a process as described above in which graphite in an amount of from 0.5 to 5% by weight, based on the total weight of the oxidic material, is added to the oxidic material or the mixture resulting from (ii).

In a preferred embodiment, the present invention therefore also provides a shaped body comprising

an oxidic material comprising

- (a) copper oxide in a proportion in the range $50 \leq x \leq 80\%$ by weight, preferably $55 \leq x \leq 75\%$ by weight,
- (b) aluminum oxide in a proportion in the range $15 \leq y \leq 35\%$ by weight, preferably $20 \leq y \leq 30\%$ by weight, and
- (c) iron oxide in a proportion in the range $1 \leq z \leq 30\%$ by weight, preferably from 2 to 25% by weight,

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in each case based on the total weight of the oxidic material after calcination, where $80 \leq x + y + z \leq 100$, in particular $95 \leq x + y + z \leq 100$,

5 metallic copper powder, copper flakes or cement powder or a mixture thereof in a proportion in the range from 1 to 40% by weight, based on the total weight of the oxidic material, and

10 graphite in a proportion of from 0.5 to 5% by weight, based on the total weight of the oxidic material,

where the sum of the proportions of oxidic material, metallic copper powder, copper flakes or cement powder or a mixture thereof and graphite makes up at least 95% by weight of the shaped body.

15 After addition of the copper powder, the copper flakes or the cement powder or the mixture thereof and, if appropriate, graphite to the oxidic material, the shaped body obtained after shaping is, if appropriate, calcined at least once for a period of generally from 0.5 to 10 hours, preferably from 0.5 to 2 hours. The temperature in this calcination step or steps is generally in the range from 200 to 600°C,
20 preferably in the range from 250 to 500°C and particularly preferably in the range from 270 to 400°C.

In the case of shaping using cement powder, it may be advantageous to moisten the shaped body obtained before calcination with water and subsequently to dry it.

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When the shaped body is used as catalyst in the oxidic form, it is prereduced by means of reducing gases, for example hydrogen, preferably hydrogen/inert gas mixtures, in particular hydrogen/nitrogen mixtures, at from 100 to 500°C, preferably from 150 to 350°C and in particular from 180 to 200°C, prior to being
30 brought into contact with the hydrogenation solution. This is preferably carried out using a mixture having a hydrogen content in the range from 1 to 100% by volume, particularly preferably in the range from 1 to 50% by volume.

In a preferred embodiment, the shaped body of the invention is activated in a
35 manner known per se by treatment with reducing media prior to use as catalyst.

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The activation is carried out either beforehand in a reduction oven or after installation in the reactor. If the reactor has been activated beforehand in the reduction oven, it is installed in the reactor and supplied directly with the hydrogenation solution under hydrogen pressure.

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A preferred area of application of the shaped bodies produced by the process of the present invention is the hydrogenation of organic compounds containing carbonyl groups in a fixed bed. However, other embodiments such as a fluidized-bed reaction using catalyst material in upward and downward swirling motion are likewise possible. The hydrogenation can be carried out in the gas phase or in the liquid phase. The hydrogenation is preferably carried out in the liquid phase, for example in the downflow mode or upflow mode.

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When the hydrogenation is carried out in the downflow mode, the liquid starting material in the reactor comprising the carbonyl compound to be hydrogenated is allowed to trickle over the catalyst bed in the reactor which is under hydrogen pressure, forming a thin liquid film on the catalyst. On the other hand, when the hydrogenation is carried out in upflow mode, hydrogen is introduced into the reactor flooded with the liquid reaction mixture and the hydrogen passes through the catalyst bed as rising gas bubbles.

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In one embodiment, the solution to be hydrogenated is pumped over the catalyst bed in a single pass. In another embodiment of the process of the present invention, part of the product is continuously taken off as product stream after passing through the reactor and, if appropriate, is passed through a second reactor as defined above. The other part of the product is combined with fresh starting material comprising the carbonyl compound and fed back into the reactor. This mode of operation will hereinafter be referred to as the circulation mode.

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If the downflow mode is chosen as embodiment of the present invention, the circulation mode is preferred. Further preference is given to carrying out the hydrogenation in the circulation mode using a main reactor and an after-reactor.

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The process of the present invention is suitable for the hydrogenation of carbonyl compounds such as aldehydes and ketones, carboxylic acids, carboxylic esters or

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carboxylic anhydrides to give the corresponding alcohols, with preference being given to aliphatic and cycloaliphatic, saturated and unsaturated carbonyl compounds. In the case of aromatic carbonyl compounds, formation of undesirable by-products by hydrogenation of the aromatic ring may occur. The carbonyl compounds may bear further functional groups such as hydroxyl or amino groups. Unsaturated carbonyl compounds are generally hydrogenated to the corresponding saturated alcohols. The term "carbonyl compounds" used in the context of the invention encompasses all compounds containing a C=O group, including carboxylic acids and their derivatives. Of course, it is also possible to hydrogenate mixtures of two or more carbonyl compounds. Furthermore, each individual carbonyl compound to be hydrogenated can also contain more than one carbonyl group.

The process of the present invention is preferably used for the hydrogenation of aliphatic aldehydes, hydroxyaldehydes, ketones, acids, esters, anhydrides, lactones and sugars.

Preferred aliphatic aldehydes are branched and unbranched, saturated and/or unsaturated aliphatic C₂-C₃₀-aldehydes, which are obtainable, for example, by means of the oxo process from linear or branched olefins having internal or terminal double bonds. It is also possible to hydrogenate oligomeric compounds containing more than 30 carbonyl groups.

Examples of aliphatic aldehydes are:

Formaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, valeraldehyde, 2-methylbutyraldehyde, 3-methylbutyraldehyde (isovaleraldehyde), 2,2-dimethylpropionaldehyde (pivalinaldehyde), caproaldehyde, 2-methylvaleraldehyde, 3-methylvaleraldehyde, 4-methylvaleraldehyde, 2-ethylbutyraldehyde, 2,2-dimethylbutyraldehyde, 3,3-dimethylbutyraldehyde, caprylic aldehyde, capric aldehyde, glutaraldehyde.

Apart from the short-chain aldehydes mentioned, long-chain aliphatic aldehydes as can be obtained, for example, by means of the oxo process from linear α -olefins, are also particularly suitable.

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Particular preference is given to enalization products such as 2-ethylhexenal, 2-methylpentenal, 2,4-diethyloctenal or 2,4-dimethylheptenal.

5 Preferred hydroxyaldehydes are C_3 - C_{12} -hydroxyaldehydes as are obtainable, for example, from aliphatic and cycloaliphatic aldehydes and ketones by aldol reaction with themselves or formaldehyde. Examples are 3-hydroxypropanal, dimethylolethanal, trimethylolethanal (pentaerythritol), 3-hydroxybutanal (acetaldehyde), 3-hydroxy-2-ethylhexenal (butyl aldol), 3-hydroxy-2-methylpentanal (propene aldol), 2-methylolpropanal, 2,2-dimethylolpropanal, 3-hydroxy-2-methylbutanal, 3-hydroxypentanal, 2-methylolbutanal, 2,2-dimethylolbutanal, hydroxypivalaldehyde. Particular preference is given to hydroxypivalaldehyde (HPA) and dimethylolbutanal (DMB).

15 Preferred ketones are acetone, butanone, 2-pentanone, 3-pentanone, 2-hexanone, 3-hexanone, cyclohexanone, isophorone, methyl isobutyl ketone, mesityl oxide, acetophenone, propiophenone, benzophenone, benzalacetone, dibenzalacetone, benzalacetophenone, 2,3-butanedione, 2,4-pentanedione, 2,5-hexanedione and methyl vinyl ketone.

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Furthermore, carboxylic acids and derivatives thereof, preferably those having 1-20 carbon atoms, can be reacted. In particular, the following may be mentioned:

carboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid, isobutyric acid, n-valeric acid, trimethylacetic acid ("pivalic acid"), caproic acid, enanthic acid, caprylic acid, capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, acrylic acid, methacrylic acid, oleic acid, elaidic acid, linoleic acid, linolenic acid, cyclohexanecarboxylic acid, benzoic acid, phenylacetic acid, o-toluic acid, m-toluic acid, p-toluic acid, o-chlorobenzoic acid, p-chlorobenzoic acid, o-nitrobenzoic acid, p-nitrobenzoic acid, salicylic acid, p-hydroxybenzoic acid, anthranilic acid, p-aminobenzoic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid, terephthalic acid;

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carboxylic esters such as the C₁-C₁₀-alkyl esters of the abovementioned carboxylic acids, in particular methyl formate, ethyl acetate, butyl butyrate, dialkyl esters of phthalic acid, isophthalic acid, terephthalic acid, adipic acid and maleic acid, e.g. the dimethyl esters of these acids, methyl (meth)acrylate, butyrolactone, caprolactone and polycarboxylic esters, e.g. polyacrylic and polymethacrylic esters and their copolymers, and polyesters, e.g. polymethyl methacrylate or terephthalic esters, and other industrial plastics; in these cases, the reactions carried out are, in particular, hydrogenolyses, i.e. the reaction of esters to form the corresponding acids and alcohols;

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fats;

carboxylic anhydrides such as the anhydrides of the abovementioned carboxylic acids, in particular acetic anhydride, propionic anhydride, benzoic anhydride and maleic anhydride;

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carboxamides such as formamide, acetamide, propionamide, stearamide, terephthalamide.

It is also possible for hydroxycarboxylic acids, e.g. lactic, malic, tartaric or citric acid, or amino acids, e.g. glycine, alanine, proline and arginine, and peptides to be reacted.

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As particularly preferred organic compounds, saturated or unsaturated carboxylic acids, carboxylic esters, carboxylic anhydrides or lactones or mixtures of two or more thereof are hydrogenated.

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The present invention therefore also provides a process as described above in which the organic compound is a carboxylic acid, a carboxylic ester, a carboxylic anhydride or a lactone.

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Examples of these compounds are, inter alia, maleic acid, maleic anhydride, succinic acid, succinic anhydride, adipic acid, 6-hydroxycaproic acid, 2-cyclododecylpropionic acid, the esters of the abovementioned acids, for

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example the methyl, ethyl, propyl or butyl ester. Further examples are γ -butyrolactone and caprolactone.

5 In a very particularly preferred embodiment, the present invention provides a process as described above in which the organic compound is adipic acid or an ester of adipic acid.

10 The carbonyl compound to be hydrogenated can be fed to the hydrogenation reactor either alone or as a mixture with the product of the hydrogenation reaction, and can be fed in in undiluted form or using an additional solvent. Suitable additional solvents are, in particular, water and alcohols such as methanol, ethanol and the alcohol formed under the reaction conditions. Preferred solvents are water, THF and NMP; particular preference is given to water.

15 The hydrogenation both in the upflow mode and in the downflow mode, in each case preferably in the circulation mode, is generally carried out at from 50 to 350°C, preferably from 70 to 300°C, particularly preferably from 100 to 270°C, and a pressure in the range from 3 to 350 bar, preferably in the range from 5 to 330 bar, particularly preferably in the range from 10 to 300 bar.

20 In a very particularly preferred embodiment, the catalysts of the present invention are used in processes for preparing hexanediol and/or caprolactone, as are described in DE 196 07 954, DE 196 07 955, DE 196 47 348 and DE 196 47 349.

25 High conversions and selectivities are achieved in the process of the present invention using the catalysts of the present invention. At the same time, the catalysts of the present invention have a high chemical and mechanical stability.

30 The present invention therefore provides quite generally for the use Cu-Al catalysts, which by the addition of lanthanum, tungsten, molybdenum, titanium and/or zirconium oxides in the production of a catalyst for increasing both the mechanical stability and the activity and selectivity of the catalyst.

35 In a preferred embodiment, the present invention provides for the use as described above of such a catalyst comprising copper as active component.

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The mechanical stability of solid-state catalysts and specifically the catalysts of the present invention is described by the parameter lateral compressive strength in various states (oxidic, reduced, reduced and suspended under water).

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The lateral compressive strength was determined for the purposes of the present patent application by means of a "Z 2.5/T 919" instrument of Zwick (Ulm). In the case of both the reduced catalysts and the used catalysts, the measurement were carried out under a nitrogen atmosphere so as to avoid reoxidation of the catalysts.

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Examples

Example 1: Production of catalyst 1

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Production of the catalyst

A mixture of 12.41 kg of a 19.34% strength copper nitrate solution, 14.78 kg of an 8.12% strength aluminum nitrate solution and 1.06 kg of a 37.58% strength iron nitrate $\times 9\text{H}_2\text{O}$ solution was dissolved in 1.5 l of water (solution 1). Solution 2 comprises 60 kg of a 20% strength anhydrous Na_2CO_3 . Solution 1 and solution 2 are introduced via separate lines into a precipitation vessel which is provided with a stirrer and contains 10 l of water heated to 80°C. The pH was brought to 6.2 by appropriate adjustment of the feed rates for solution 1 and solution 2.

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While keeping the pH constant at 6.2 and maintaining a temperature of 80°C, all of solution 1 was reacted with sodium carbonate. The suspension formed in this way was subsequently stirred for another 1 hour, with the pH being increased to 7.2 by occasional addition of dilute nitric acid or sodium carbonate solution 2. The suspension was filtered and washed with distilled water until the nitrate content of the washings was < 10 ppm.

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The filter cake was dried at 120°C for 16 hours and subsequently calcined at 300°C for 2 hours. The catalyst powder obtained in this way is precompacted with 1% by weight of graphite. The compact obtained is mixed with 5% by weight of Cu

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flakes from Unicoat and subsequently with 2% by weight of graphite and pressed to form pellets having a diameter of 3 mm and a height of 3 mm. The pellets were finally calcined at 350°C for 2 hours.

- 5 The catalyst produced in this way has the chemical composition 57% CuO/28.5% Al₂O₃/9.5% Fe₂O₃/5% Cu.

The lateral compressive strength in the oxidic state was 117 N and in the reduced state was 50 N, as shown in Table 1.

- 10 Example 2: Hydrogenation of dimethyl adipate over catalyst 1

Dimethyl adipate was hydrogenated continuously in the downflow mode with recirculation (feed/recycle ratio = 10/1) at a WHSV of 0.3 kg/(l*h), a pressure of 200 bar and reaction temperatures of 190°C in a vertical tube reactor charged with 200 ml of catalyst 1. The experiment was carried out for a total time of 7 days. GC analysis found ester conversions of 99.9%, a hexanediol selectivity of 97.5% in the reaction product at 190°C. After removal from the reactor, the catalyst was found to be still completely intact and had a high mechanical stability. The experimental results are summarized in Table 1.

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Example 3: Production of the comparative catalyst without iron

The comparative catalyst was produced by a method analogous to that for catalyst 2, but without the addition of the iron nitrate solution: 14.5 kg of a 19.34% strength copper nitrate solution and 14.5 kg of an 8.12% strength aluminum nitrate solution (solution 1) are precipitated by means of sodium carbonate solution in a manner analogous to catalyst 1.

25 The catalyst produced in this way has the chemical composition 66.5% CuO/28.5% Al₂O₃/5% Cu. The lateral compressive strength in the oxidic and reduced states is shown in Table 1.

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Example 4: Hydrogenation of dimethyl adipate over the comparative catalyst

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Dimethyl adipate was hydrogenated continuously in the downflow mode with recirculation (feed/recycle ratio = 10/1) at a WHSV of 0.3 kg/(l*h), a pressure of 200 bar and reaction temperatures of 190°C in a vertical tube reactor charged with 200 ml of catalyst 2. The experiment was carried out for a total time of 7 days. GC analysis found ester conversions of 80.2% in each case and hexanediol contents of 86.6% in the reaction product at 220°C and 240°C, respectively. After removal from the reactor, the catalyst was found to be still completely intact and had a high mechanical stability. The experimental results are summarized in Table 1.

The data in Table 1 below show that the catalysts of the present invention have considerably higher hydrogenation activities, i.e. higher conversions of dimethyl adipate, at 190°C than the comparative catalyst, and also give higher selectivities to the desired product, i.e. higher contents of the target products hexanediol in the output from the reactor.

Table 1

Catalyst	Reaction temperature [°C]	Conversion of dimethyl adipate [%]	Hexanediol selectivity [%]	Lateral compressive strength (N) oxid./red.
Catalyst 1	190	99.9	97.5	117/50
Comparative catalyst	190	80.2	86.6	77/45

We claim:

1. A process for the hydrogenation of an organic compound containing at least one carbonyl group, which comprises bringing the organic compound in the presence of hydrogen into contact with a shaped body which can be produced by a process in which
- (i) an oxidic material comprising copper oxide, aluminum oxide and iron oxide is made available,
- (ii) pulverulent metallic copper, copper flakes, pulverulent cement, graphite or a mixture thereof is added to the oxidic material, and
- (iii) the mixture resulting from (ii) is shaped to form a shaped body.
2. The process according to claim 1, wherein the oxidic material comprises
- (a) copper oxide in a proportion in the range $50 \leq x \leq 80\%$ by weight, preferably $55 \leq x \leq 75\%$ by weight,
- (b) aluminum oxide in a proportion in the range $15 \leq y \leq 35\%$ by weight, preferably $20 \leq y \leq 30\%$ by weight, and
- (c) iron oxide in a proportion in the range $1 \leq z \leq 30\%$ by weight, preferably $2 \leq z \leq 25\%$ by weight,
- in each case based on the total weight of the oxidic material after calcination, where $80 \leq x + y + z \leq 100$, in particular $95 \leq x + y + z \leq 100$, and cement is not included as part of the oxidic material in the above sense.
3. The process according to claim 1 or 2, wherein the pulverulent metallic copper, the copper flakes, the pulverulent cement or graphite or the mixture thereof is added in an amount in the range from 1 to 40% by weight, based on the total weight of the oxidic material.

4. The process according to any of claims 1 to 4, wherein graphite is added in an amount in the range from 0.5 to 5% by weight, based on the total weight of oxidic material, to the oxidic material or the mixture resulting from (ii).
5. The process according to any of claims 1 to 4, wherein the organic compound is a carboxylic acid, a carboxylic ester, a carboxylic anhydride or a lactone.
6. The process according to claim 6, wherein the organic compound is adipic acid or an ester of adipic acid.
7. A shaped body comprising
an oxidic material comprising
- (a) copper oxide in a proportion in the range $50 \leq x \leq 80\%$ by weight, preferably $55 \leq x \leq 75\%$ by weight,
- (b) aluminum oxide in a proportion in the range $15 \leq y \leq 35\%$ by weight, preferably $20 \leq y \leq 30\%$ by weight, and
- (c) iron oxide in a proportion in the range $1 \leq z \leq 30\%$ by weight, preferably $2 \leq z \leq 25\%$ by weight,
- in each case based on the total weight of the oxidic material after calcination, where $80 \leq x + y + z \leq 100$, in particular $95 \leq x + y + z \leq 100$,
- metallic copper powder, copper flakes or cement powder or graphite or a mixture thereof in a proportion in the range from 1 to 40% by weight, based on the total weight of the oxidic material, and
- graphite in a proportion of from 0.5 to 5% by weight, based on the total weight of the oxidic material,
- where the sum of the proportions of oxidic material, metallic copper powder or cement powder or a mixture thereof and graphite makes up at least 95% by weight of the shaped body.