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Copper/zinc oxide/aluminum oxide-containing catalysts

The present invention relates to copper-containing catalysts having a comparatively high BET total surface area and a defined pore radius distribution, to a process for the preparation thereof, starting from aqueous solutions containing a copper salt and salts of other elements, from which solutions a coprecipitate is obtained with the aid of a basic precipitant, the coprecipitate then being washed and calcined after drying, and also to the use thereof.

Copper-containing catalysts are used, as are nickel catalysts, to a considerable extent in industrial processes. They play a significant role, for example, in hydrogenation and dehydrogenation processes. In this case, the starting material to be converted is passed to the fixed catalyst either in the gaseous state (gas phase procedure) or in the liquid state (liquid phase procedure). The catalyst can also be used in a finely divided state as a slurry (suspension procedure).

Catalysts which, along with copper, also contain chromium have a very broad application range. These catalysts are also known under the term copper chromite catalysts or Adkins catalysts.

However, the use of Adkins catalysts is not without problems since chromium(VI) compounds, which are considered to be carcinogenic and require appropriate safety measures during handling, are used during their preparation. Moreover, relatively large amounts of waste water are produced in the course of the preparation, which waste water is highly polluted with copper compounds, chromium(VI) compounds and ammonium compounds. Such waste water is undesired, since copper compounds and also chromium(VI) compounds have a highly toxic effect on microorganisms and must be removed from the waste water by a complex treatment process.

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Besides copper chromite catalysts, nickel catalysts have proven suitable in many respects. However, because of their very high activity, nickel catalysts lead, in particular at relatively high reaction temperatures, to uncontrolled side reactions and secondary reactions, for example cleavages, transalkylations and/or rearrangements. However, this favors the formation of undesired byproducts and/or secondary products.

Copper catalysts are also known which do not contain chemically bound chromium. However, these catalysts do not have the properties of either the Adkins catalyst or of the nickel catalysts.

Thus, German Offenlegungsschrift 2,056,612 describes a catalyst composed of solid solutions of the series $(Cu_xZn_y)Al_2(OH)_{16}CO_3 \cdot 4H_2O$, where x and y can have values from 0.5 to 5.5 and the sum of x and y is 6. The solid solutions are obtained by precipitation at a pH of 4.5 to 5.5 by adding a basic precipitant, for example an aqueous Na_2CO_3 solution, to an aqueous solution containing copper nitrate, zinc nitrate and aluminum nitrate.

The catalyst in the unreduced form containing CuO, ZnO and Al_2O_3 is used in the reaction of a gas mixture composed of carbon monoxide, carbon dioxide and hydrogen to give methanol.

EP 0,125,689 relates to a catalyst for methanol synthesis containing CuO, ZnO and Al_2O_3 having an atomic ratio Cu/Zn between 2.8 and 3.8 (corresponding to 26.9 to 36.5 parts by weight of ZnO per 100 parts by weight of CuO) and an Al_2O_3 fraction of 8 to 12% by weight. Al_2O_3 is used as colloidal aluminum hydroxide in the preparation, Cu and Zn are introduced into the catalyst by precipitation from metal salt solutions. 20 to 40% of the pores have a diameter of 2.0 to 7.5 nm (20 to 75 Å) - corresponding to a pore radius r_p of 1.0 to 3.75 nm (10 to 37.5 Å) - and 80

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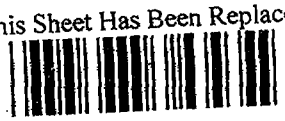
to 60% of the pores, relative in each case to the total number of pores, have a diameter > 7.5 nm (75 Å) - corresponding to a pore radius r_p > 3.75 nm (37.5 Å). The catalysts described in more detail in the examples have, in the unreduced state, a BET surface area of 100 to 127 m^2/g and 32 to 42% of the pores with a diameter of 2.0 to 7.5 nm (r_p = 1.0 to 3.75 nm) and 68 to 57% of the pores with a diameter > 7.5 nm (r_p > 3.75 nm).

As the preceding remarks confirm, there is a requirement for a catalyst which can be used, at least within a specific application area, both in place of an Adkins catalyst and also in place of a nickel catalyst. Moreover, problems in the preparation of this catalyst, such as handling carcinogenic chromium(VI) compounds, production of waste water containing pollutants and disposal of chromium-containing used catalysts, are to be avoided. Furthermore, the novel catalyst is to ensure, in particular at relatively high temperatures, a high conversion with high activity and a high selectivity of the reaction, that is to say the undesired side reactions and secondary reactions typical of nickel catalysts are to be prevented as far as possible.

This applies, inter alia, especially to an important area of application for copper chromite or Adkins catalysts and also nickel catalysts, namely the catalytic hydrogenation of aldehydes to give the corresponding alcohols. In this area, the novel catalyst is to be capable of replacing not only a nickel catalyst, but also a copper chromite or Adkins catalyst.

This object is achieved by a catalyst containing, per 100 parts by weight of CuO, 40 to 130 parts by weight of ZnO, 2 to 50 parts by weight of Al_2O_3 and, possibly, 0.5 to 8 parts by weight of an oxide of Mn, Mo, V, Zr and/or of an alkaline earth metal, having a BET total surface area of 80 to 175 m^2/g of the catalyst in the unreduced

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state, 75 to 95% of the BET total surface area being formed by pores having a radius $r_p \leq 15$ nm.

A further characteristic of the catalyst is a relatively large active copper metal surface area. In the unreduced catalyst, this is 30 to 125, in particular 35 to 100, preferably 40 to 85, m^2/g of Cu and thus exceeds the active copper metal surface area of corresponding copper chromite catalysts. The method of determination is to be taken from M.J. Juys, P.H. van Oeffelt, W.G.J. Brouwe, A.P. Pijpers and J.J.F. Scholten, Applied Catalysis, 46 (1989), pages 161 to 173.

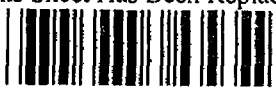
The catalyst contains, per 100 parts by weight of CuO, 40 to 130, in particular 45 to 100, preferably 45 to 80, parts by weight of ZnO and 2 to 50, in particular 3 to 40, preferably 4 to 30, particularly preferably 4 to 11, parts by weight of Al_2O_3.

If necessary, the catalyst also comprises additional substances. These include oxides of manganese, molybdenum, vanadium, zirconium and/or of an alkaline earth metal. Per 100 parts by weight of CuO, they are present in amounts of 0.5 to 8, in particular 1 to 6, preferably 2 to 4, parts by weight calculated as MnO, MoO_3, V_2O_5, ZrO_2 and MeO, where Me is an alkaline earth metal.

Additional substances which are particularly suitable are manganese oxide and/or an alkaline earth metal oxide. The alkaline earth metal oxide can be Mg oxide, Ca oxide or Ba oxide, in particular Ca oxide or Ba oxide, preferably Ba oxide.

An essential characteristic of the catalyst according to the invention is the comparatively high BET total surface area. This is 80 to 175, in particular 85 to 160, preferably 90 to 155, m^2/g of catalyst in the unreduced state.

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The BET total surface area is taken to mean the surface area determined by adsorption of nitrogen by the Brunauer, Emmett and Teller method (BET). The method for the determination of the BET total surface area is described in J. Amer. Chem. Soc., 60, (1938) 309.

An essential characteristic of the catalyst is a defined distribution of the pore radii, expressed by a high proportion of the BET total surface area which is formed by the pores having a radius $r_p \leq 15$ nm (150 Å). Its proportion is 75 to 95%, in particular 80 to 92%, preferably 84 to 90% of the BET total surface area.

50 to 85%, in particular 60 to 80%, of the BET total surface area is formed by pores having a radius $r_p \leq 9$ nm (90 Å).

5 to 45%, in particular 15 to 40%, preferably 18 to 30% of the BET total surface area comprises pores, the radius of which is $r_p = 9$ to 15 nm.

It may again be noticed at this point that the preceding details of the BET total surface area relate in each case to the catalyst in the unreduced form.

The determination of the pore radii is carried out by evaluation of the desorption isotherms with the aid of the Kelvin equation according to C. Pierce, J. Phys. Chem. 57, (1953) 149. The details with regard to the pore radii are likewise based on the unreduced catalyst.

The catalyst can, if desired, also contain a support in addition to the abovementioned constituents. Per 100 parts by weight of CuO, it contains 2 to 80, in particular 4 to 60, preferably 5 to 35, parts by weight of support. The supports used can be conventional materials which are insoluble in water. Suitable support materials are SiO_2, kieselguhr, silica gel and Al_2O_3, in particular

Al_2O_3.

94 to 97% by weight of unreduced, calcined catalyst comprises CuO, ZnO, Al_2O_3 and additional substances, including oxides of manganese, molybdenum, vanadium, zirconium and/or of an alkaline earth metal and also, if required, a support. The remaining 3 to 6% by weight is composed of physically and/or chemically bound water, any hydroxyl groups still present, oxides of a composition other than that corresponding to the formula on which the calculation is based, carbonate fractions and relatively small amounts of substances which are used in the preparation, in particular precipitants.

The invention further relates to a catalyst in reduced form. The CuO is converted by the reduction into metallic Cu, whereby the catalyst is activated.

In the reduced form, the catalyst contains, per 100 parts by weight of Cu, 48 to 163, in particular 56 to 125, preferably 56 to 100, parts by weight of ZnO, 2.4 to 63, in particular 3.7 to 50, preferably 5.0 to 37.5, particularly preferably 5 to 13.8, parts by weight of Al_2O_3 and, possibly, 0.6 to 10, in particular 1.2 to 7.5, preferably 2.4 to 5.0, parts by weight of an oxide of Mn, Mo, V, Zr and/or of an alkaline earth metal.

Catalysts are particularly suitable which also contain Mn oxide or Ba oxide along with Cu, ZnO and Al_2O_3. The catalyst can additionally contain a further support material. A catalyst of this type contains, per 100 parts by weight of Cu, 2.4 to 100, in particular 4.8 to 75, preferably 6 to 44, parts by weight of a support. The support materials can be substances which are insoluble in water, in particular SiO_2 such as kieselguhr or silica gel and/or Al_2O_3, preferably Al_2O_3.

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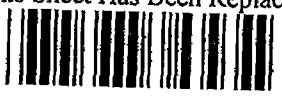
The remaining parameters, namely the BET total surface area and the pore radius distribution, roughly correspond to those identified for the unreduced catalyst.

The process for the preparation of the catalyst according to the invention starts with an aqueous solution containing salts of copper, zinc, aluminum and possibly Mn, Mo, V, Zr and/or of an alkaline earth metal. This solution, also termed mixed salt solution below, contains 10 to 100, in particular 20 to 80, preferably 30 to 60, g of Cu/l, 10 to 50, in particular 15 to 40, preferably 10 to 30, g of Zn/l and Al corresponding to 2 to 80, in particular 5 to 60, preferably 10 to 40, g of Al_2O_3/l. If required, the mixed salt solution also has 3 to 80, in particular 5 to 50, preferably 10 to 30, g of Mn, Mo, V, Zr and/or of an alkaline earth metal, calculated as MnO, MoO_3, V_2O_5, ZrO_2 and MeO, in which Me is an alkaline earth metal.

The mixed salt solution is prepared by dissolving water-soluble inorganic, organic or complex salts of the abovementioned elements in water. Highly suitable salts are the sulfates, chlorides, acetates, propionates, butyrates and nitrates. It has proved particularly expedient to use sulfates, chlorides, acetates and nitrates, in particular nitrates, in the preparation of the mixed salt solution.

In order to prevent a partial, undesired hydrolysis and to influence the precipitation favorably, it is recommended to maintain a certain excess of free acid in the mixed salt solution. The mixed salt solution, if necessary by addition of acid, is expediently adjusted to a pH below 4.5, in particular to a pH between 2.0 and 4.0. By this means it is ensured that the precipitation proceeds under reproducible conditions, and, moreover, that a precipitation product as uniform as possible is obtained.

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The acids used can be mineral acids such as hydrochloric acid, sulfuric acid and nitric acid. Nitric acid is particularly suitable.

The mixed salt solution and the aqueous solution of a basic precipitatant are separately, but simultaneously, possibly in the presence of a support, brought together with mixing.

The precipitant used is an aqueous solution of a basic compound, in particular an aqueous solution of an alkali metal carbonate, alkali metal hydrogen carbonate, alkali metal hydroxide, ammonium hydroxide or ammonium carbonate. Mixtures thereof can also be used. An aqueous solution containing Na_2CO_3 and/or $NaHCO_3$ is particularly suitable. The precipitant is to have a pH of 7.5 to 13, in particular 8 to 12, preferably 9 to 11.

The aqueous solution contains 0.1 to 4.0, in particular 0.6 to 3.0, preferably 1.6 to 2.4, equivalents of basic compound/l of solution. Very good results are obtained with aqueous solutions which contain 0.3 to 1.5, in particular 0.8 to 1.2, mol of alkali metal carbonate/l of solution.

To ensure as complete a precipitation as possible and at the same time to obtain a particularly homogeneous coprecipitate composed of the corresponding basic compounds of copper, zinc, aluminum, and, possibly, of manganese, molybdenum, vanadium, zirconium and/or of an alkaline earth metal, the basic compound is used in excess. The stoichiometric excess is generally 5 to 60%, in particular 10 to 50% of the basic compound. The use of a 15 to 30% excess of basic compound has proved to be particularly expedient. The excess relates in each case to the amount of basic compound which is required for complete precipitation of the metals contained in the mixed salt solution.

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The stoichiometric excess should be such that, although on the one hand the precipitation of as homogeneous a coprecipitate as possible is indeed assured, on the other hand a precipitation of the metal ions contained in the mixed salt solution occurs to the desired extent in each case, preference being given to the most complete precipitation possible.

The precipitation is caused by bringing together the mixed salt solution and the precipitant separately, but simultaneously, continuously or discontinuously with intensive mixing.

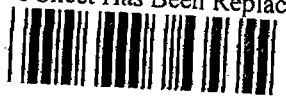
The precipitation of the coprecipitate composed of the basic compounds is brought about by bringing together the mixed salt solution and the precipitant comparatively slowly. The precipitation time should be at least 10, in particular at least 15, preferably at least 20, minutes.

The mixed salt solution and the solution of the basic precipitant are heated to a predetermined temperature. This temperature should roughly correspond to the temperature at which the precipitation is carried out.

It has generally proved to be expedient to keep to a precipitation time of 10 to 100, in particular 15 to 95, preferably 20 to 90, minutes. The precipitation time can be altered by selection of an appropriate addition rate of mixed salt solution and precipitant, in particular in the case of discontinuous precipitation, whereas, in the case of the continuous procedure, in addition to the addition rates of the mixed salt solution and precipitant, the throughput relative to the reaction volume is also to be considered.

During the precipitation, a constant pH is employed within a pH range of 6.5 to 8.5, in particular 7.6 to 8.0. Variations the pH should be kept as small as

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possible, in order to ensure the preparation of a particularly homogeneous coprecipitate. The variations in pH should be limited by an interval of -0.5 to +0.5, preferably -0.2 to +0.2.

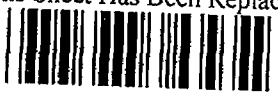
The precipitation is carried out at temperatures above 70°C, in particular in a range of 75 to 95°C, preferably 75 to 85°C. For this purpose, it is sufficient to adjust the substances participating in the precipitation, namely the mixed salt solution and the precipitant, to an appropriately high temperature. During the precipitation, the temperature should be held as constant as possible. The deviations from the predetermined temperature should not exceed ± 2°C, in particular ± 1°C. Larger variations in the precipitation temperature can influence the quality, for example particle size, homogeneity and structure of the coprecipitate in a disadvantageous manner.

Subsequent to the precipitation, the coprecipitate, possibly after further brief stirring, is separated off from the mother liquor, for example by decanting and/or filtering, and is carefully washed. The amount of wash water used, the flow rate and temperature of the wash water as well as the duration of the washing process influence the elimination of undesired constituents from the coprecipitate, in particular the dissolving-out of nitrate ions and alkali metal ions.

Increasing amounts of wash water, high temperatures of the wash water and long duration of the wash process promote a particularly extensive dissolving-out, whereas relatively low amounts of wash water, low temperatures of the wash water and short duration of the wash process lead to a reduced dissolving-out.

It is generally sufficient to maintain a temperature of 55 to 85°C, in particular 60 to 75°C during the washing.

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Higher wash temperatures can have disadvantageous effects on the quality of the precipitate. The use of temperatures which are too low can lead to undesired constituents not being eliminated to the required extent from the coprecipitate. This can also have an unfavorable effect on the quality of the useful product.

Generally, 5 to 50, in particular 10 to 30, preferably 15 to 25, liters of wash water are used per kg of coprecipitate.

The duration of the wash process must be sufficiently long. It should be at least 60, in particular at least 70, preferably at least 80, minutes. A sufficient washing duration is generally 80 to 140, in particular 85 to 130, preferably 90 to 120, minutes.

The wash process can be carried out in a single step or in a plurality of successive stages, by appropriately apportioning the total amount of wash water required. Which procedure is preferred depends on the individual case. In general, both a single stage and a multistage process lead to the desired result. A multistage wash process can be advantageous in many cases, since less wash water is usually required than in a single stage process.

Monitoring of the wash process is facilitated by determination of the compounds dissolved out, present in the wash water, such as $NaNO_3$. Monitoring in this manner can be dispensed with if the washing process is performed under standardized and controlled conditions, for example with a preset amount of wash water, temperature and duration.

If required, the washed material can be converted into a particulate form. Proven processes, such as, for example, extrusion, can be used for shaping the material.

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Drying is carried out in stages at elevated temperatures, preferably at increasing temperatures. It has proved sufficient to carry out the drying at temperatures of 50 to 120°C, in particular 55 to 100°C, preferably 60 to 90°C with the use of conventional processes, such as disposing the material to be dried in a fixed bed or in a moving bed, for example in a fluidized layer.

Drying is carried out until a residual water content of about 2 to 15%, in particular 3 to 10% by weight of water, relative to the dried coprecipitate, is attained.

The subsequent calcination is carried out at 250 to 450°C, in particular 320 to 400°C over a period of 3 to 10, in particular 4 to 8, hours. The calcined catalyst can be used either directly in powder form for suspension hydrogenations or after shaping, such as tableting or pelleting, as a fixed-bed catalyst.

The calcined catalyst is reduced (activated) to prepare the actual catalyst active in hydrogenation. For this purpose, the calcined, unreduced catalyst is treated at 130 to 190°C, possibly at elevated pressure, with hydrogen. It has proved particularly expedient to carry out the reduction with a hydrogen/nitrogen mixture. It is recommended to use a hydrogen/nitrogen mixture containing 1 to 5% by volume of hydrogen. As a result of the treatment with hydrogen, metallic Cu is formed from CuO.

The catalyst according to the invention can be used advantageously for hydrogenations of aldehydes, such as aromatic and aliphatic straight-chain and/or branched aldehydes, in the liquid phase but also in the gaseous phase. An advantage is that high conversions and good selectivities are achieved even at comparatively high temperatures, without formation of undesired byproducts having to be taken into consideration to any significant extent. In this manner, aldehydes and aldehyde

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derivatives of low reactivity, for example unsaturated aliphatic aldehydes, can also be hydrogenated to give the corresponding alcohols without difficulty.

The examples below document the present invention without restricting it.

Experimental Section

Example 1

Preparation of a catalyst containing CuO, ZnO and Al_2O_3.

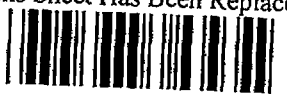
4,356 g of $Cu(NO_3)_2 \cdot 3H_2O$, 2,615 g of $Zn(NO_3)_2 \cdot 6H_2O$ and 895.8 g of $Al(NO_3)_3 \cdot 9H_2O$ are dissolved in 18 liters of deionized water (mixed salt solution). The mixed salt solution is heated to 80°C.

The solution of the basic precipitant is obtained by dissolving 3,750 g of Na_2CO_3 in 30 liters of deionized water. This solution is likewise heated to 80°C.

8 liters of deionized water are placed in a precipitation vessel which is equipped with a stirrer and are heated to 80°C with stirring. The mixed salt solution and the solution of the basic precipitant are run into the precipitation vessel separately, but simultaneously, in the course of 20 minutes with vigorous stirring. The flow rates of the two solutions are matched to each other so that a pH of 7.5 to 7.8 is maintained in the precipitation vessel. The temperature in the precipitation vessel is held constant at 80°C.

After completion of the precipitation, the suspension present in the precipitation vessel is stirred for a further 2 minutes. The precipitate (coprecipitate) is then separated off from the mother liquor by filtration and is then washed within a period of 2 hours with

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120 liters of hot, 60 to 65°C, water. The washed filter-cake is dried either in extruded form or by spray drying to a final moisture content of ≤ 5% by weight of H_2O, relative to the catalyst mass.

The dried precipitation product is calcined for 4 hours in a stream of N_2 at 380°C.

The calcined catalyst contains 47.5% by weight of Cu. It contains, per 100 parts by weight of CuO, 49.5 parts by weight of ZnO, 8.4 parts by weight of Al_2O_3, 3.7 parts by weight of CO_2 and 0.12 part by weight of Na_2O.

The BET total surface area is 128 m^2/g of catalyst in the unreduced state. 85% of the BET total surface area is formed by pores having a radius $r_p \leq 15$ nm. The copper metal surface area of the reduced catalyst is 68 m^2/g of Cu.

Example 2

Preparation of a catalyst containing CuO, ZnO, Al_2O_3 and BaO.

4,356 g of $Cu(NO_3)_2 \cdot 3H_2O$, 2,615 g of $Zn(NO_3)_2 \cdot 6H_2O$, 895.8 g of $Al(NO_3)_3 \cdot 9H_2O$ and 73.2 g of $Ba(NO_3)_2$ are dissolved in 18 liters of deionized water (mixed salt solution). The mixed salt solution is heated to 80°C.

The solution of the basic precipitant is obtained by dissolving 3,750 g of Na_2CO_3 in 30 liters of deionized water. This solution is likewise heated to 80°C.

The procedure as given in Example 1 is then followed exactly.

The calcined catalyst contains 46.5% by weight of Cu. It contains, per 100 parts by weight of CuO, 49.8 parts by

weight of ZnO, 8.2 parts by weight of Al_2O_3, 3.6 parts by weight of CO_2, 0.12 part by weight of Na_2O and 2.0 parts by weight of BaO. The BET total surface area is 127 m^2/g of catalyst in the unreduced state. 88% of the BET total surface area is formed by pores having a radius $r_p \leq 15$ nm. The copper metal surface area of the reduced catalyst is 65 m^2/g of Cu.

Example 3

Preparation of a catalyst containing CuO, ZnO, Al_2O_3 and MnO.

1,936 g of $Cu(NO_3)_2 \cdot 3H_2O$, 1,152.4 g of $Zn(NO_3)_2 \cdot 6H_2O$, 234.2 g of $Al(NO_3)_3 \cdot 9H_2O$ and 78.9 g of $Mn(NO_3)_2 \cdot 4H_2O$ are dissolved in 10.2 liters of deionized water (mixed salt solution). The mixed salt solution is heated to 80°C.

The solution of the basic precipitant is obtained by dissolving 1,620 g of Na_2CO_3 in 15.4 liters of deionized water. This solution is likewise heated to 80°C.

6 liters of deionized water are placed in a precipitation vessel which is equipped with a stirrer and are heated to 80°C with stirring. The mixed salt solution and the solution of the basic precipitant are run into the precipitation vessel separately, but simultaneously, in the course of 17 minutes with vigorous stirring.

The procedure given in Example 1 is then followed exactly.

The calcined catalyst contains 47.3% by weight of Cu. It contains, per 100 parts by weight of CuO, 53.3 parts by weight of ZnO, 5.3 parts by weight of Al_2O_3, 2.9 parts by weight of MnO, 3.2 parts by weight of CO_2 and 0.15 part by weight of Na_2O.

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The BET total surface area is 95 m^2/g of catalyst in the unreduced state. 85% of the BET total surface area is formed by pores of a radius $r_p \leq 15$ nm. The copper metal surface area of the reduced catalyst is 54 m^2/g of Cu.

Example 4

Preparation of a catalyst containing CuO, ZnO, Al_2O_3, MnO and support.

1,459 g of $Cu(NO_3)_3 \cdot 3H_2O$, 700.7 g of $Zn(NO_3)_2 \cdot 6H_2O$, 176.5 g of $Al(NO_3)_3 \cdot 9H_2O$ and 59.4 g of $Mn(NO_3)_2 \cdot 4H_2O$ are dissolved in 7.7 liters of deionized water (mixed salt solution). The mixed salt solution is heated to 85°C.

The solution of the basic precipitant is obtained by dissolving 1,505 g of Na_2CO_3 in 14.2 liters of deionized water. This solution is likewise heated to 85°C.

48 g of finely divided Al_2O_3 (commercial product "Type H" from Martinswerk/Bergheim), as a support, and 4 liters of deionized water are placed in a precipitation vessel which is equipped with a stirrer, and the mixture is heated to 85°C with stirring. The mixed salt solution and the solution of the basic precipitant are run into the precipitation vessel separately, but simultaneously, in the course of 24 minutes with vigorous stirring. The flow rates of the two solutions are matched to each other so that a pH of 7.7 to 8.0 is maintained in the precipitation vessel. The temperature in the precipitation vessel is held constant at 85°C. After the precipitation is completed, the procedure as given in Example 1 is followed, except that the dried precipitation product containing the support is calcined for 5 hours in the N_2 stream at 380°C.

The calcined catalyst contains 45.6% by weight of Cu. It contains per 100 parts by weight of CuO, 43.2 parts by

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weight of ZnO, 13.3 parts by weight of Al_2O_3, 2.8 parts by weight of MnO, 3.7 parts by weight of CO_2 and 0.1 part by weight of Na_2O. The BET total surface area is 117 m^2/g of unreduced catalyst. 83% of the BET total surface area is formed by pores having a radius $r_p \leq 15$ nm. The copper metal surface area of the reduced catalyst is 76 m^2/g of Cu.

Example 5

Hydrogenation of n-butanal

3 liters of the catalyst prepared according to Example 1 are placed in pelleted form (6 x 5 mm pellets) in a jacketed tube reactor having an internal diameter of 38 mm.

The catalyst-containing layer is heated to 160°C and, for activation, an N_2 stream containing 3% by volume of H_2 is passed through the catalyst layer at normal pressure at a gas flow rate of 1,000 l/liter of catalyst x hour ($V_{gas\ stream}/V_{catalyst} \times h$). The feed of the N_2 stream containing 3% by volume of H_2 is ended after 24 hours and the temperature in the catalyst layer is reduced to 143°C.

n-Butanal is evaporated in an evaporator operated at 130°C, with feeding of an H_2-gas stream (98% hydrogen) which is adjusted to a pressure of 0.35 MPa and a flow rate of 10.2 Nm^3/h. The resulting gas mixture is heated in a heater to 143°C and is fed to the solid catalyst in the jacketed tube reactor.

Over a period of 8 hours each, 600, 1,200 and 1,800 ml of liquid n-butanal/h are initially used (corresponding to a V/Vh of 0.2, 0.4 and 0.6, where V/Vh is the volume of liquid n-butanal/volume of catalyst x hour). An hourly quantity of 3,000 ml of liquid n-butanal (V/Vh = 1) is then fed to the reaction (in evaporated form).

The reaction product produced has the composition below, determined by gas chromatographic analysis.

n-Butanal	0.1 to 0.3% by weight
n-Butanol	99.5 to 99.7% by weight
i-Butanol	0.04% by weight
Remainder byproducts	

The CO number is 1.0 [mg of KOH/g].

Example 6

Hydrogenation of 2-ethylhexenal

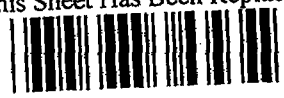
3 liters of the catalyst prepared according to Example 4 are placed in tableted form (6 x 5 mm tablets) in a jacketed tube reactor having an internal diameter of 38 mm.

The catalyst is activated as described in Example 5 and the temperature in the catalyst layer is then reduced to 143°C.

1,500 ml of 2-ethylhexenal/hour (corresponding to V/Vh = 0.5, where V/Vh is the volume of liquid 2-ethylhexenal/volume of catalyst x hour) are evaporated in an evaporator operated at 100°C with feed of an H_2 stream (98% hydrogen) which is adjusted to a pressure of 0.15 MPa and a flow rate of 4.4 Nm^3/h. The resulting gas mixture is heated in a heater to 140°C and is fed to the solid catalyst in the jacketed tube reactor.

The reaction is carried out for 2,160 hours without interruption, without any marked impairment of the course of reaction being observed.

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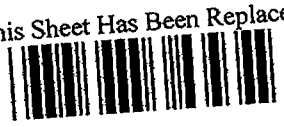


The composition of the starting material and of the reaction product (determined by gas chromatographic analysis) are compiled in the table below.

Table

	Starting material (% by weight)	Reaction product (% by weight)
C_3-C_7-hydrocarbon	0.1%	0.3 - 0.4
n-butanal	1.6%	-
n/i-butanol	0.7%	2.2
2-ethylhexanal	0.6	0.4
2-ethylhexenal	91.0	<0.01
2-ethylhexanol	4.0	96.5
heavy ends	approx. 1.5	approx. 0.5

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Patent Claims

1. A catalyst containing, per 100 parts by weight of CuO, 40 to 130 parts by weight of ZnO, 2 to 50 parts by weight of Al_2O_3 and, possibly, 0.5 to 8 parts by weight of an oxide of Mn, Mo, V, Zr and/or of an alkaline earth metal, having a BET total surface area of 80 to 175 m^2/g of catalyst in the unreduced state, 75 to 95% of the BET total surface area being formed by pores having a radius $r_p \leq 15$ nm.

2. The catalyst as claimed in claim 1, wherein the active copper metal surface area of the reduced catalyst is 30 to 125, in particular 35 to 100, preferably 40 to 85, m^2/g of Cu.

3. The catalyst as claimed in claim 1 or 2, which contains, per 100 parts by weight of CuO, 45 to 100, in particular 45 to 80, parts by weight of ZnO and 3 to 40, in particular 4 to 30, preferably 4 to 11, parts by weight of Al_2O_3.

4. The catalyst as claimed in one or more of claims 1 to 3, which contains, per 100 parts by weight of CuO, 0.5 to 8, in particular 1 to 6, preferably 2 to 4, parts by weight of an oxide of Mn, Mo, V, Zr and/or of an alkaline earth metal, in particular an oxide of Mn and/or of an alkaline earth metal.

5. The catalyst as claimed in one or more of claims 1 to 4, wherein as alkaline earth metal oxide it contains Mg oxide, Ca oxide or Ba oxide, in particular Ca oxide or Ba oxide, preferably Ba oxide.

6. The catalyst as claimed in one or more of claims 1 to 5, wherein the BET total surface area is 85 to 160, in particular 90 to 155, m^2/g of catalyst in the unreduced state.

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7. The catalyst as claimed in one or more of claims 1 to 6, wherein 80 to 92%, preferably 84 to 90% of the BET total surface area is formed by pores having a radius $r_p \leq 15$ nm.

8. The catalyst as claimed in one or more of claims 1 to 7, wherein 50 to 85%, in particular 60 to 80% of the BET total surface area is formed by pores having a radius $r_p \leq 9$ nm.

9. The catalyst as claimed in one or more of claims 1 to 8, wherein 5 to 45%, in particular 15 to 40%, preferably 18 to 30% of the BET total surface area is formed by pores having a radius $r_p = 9$ to 15 nm.

10. The catalyst as claimed in one or more of claims 1 to 9, which contains, per 100 parts by weight of CuO, in addition 2 to 80, in particular 4 to 60, preferably 5 to 35, parts by weight of a support which is insoluble in water, in particular SiO_2 such as kieselguhr or silica gel and/or Al_2O_3, preferably Al_2O_3.

11. The catalyst as claimed in one or more of claims 1 to 10, which, in reduced form, contains, per 100 parts by weight of Cu, 48 to 163 parts by weight of ZnO, 2.4 to 63 parts by weight of Al_2O_3 and possibly 0.6 to 10 parts by weight of an oxide of Mn, Mo, V, Zr and/or of an alkaline earth metal.

12. The catalyst as claimed in claim 11, which contains, per 100 parts by weight of Cu, 56 to 125, in particular 56 to 100, parts by weight of ZnO, 3.7 to 50, in particular 5.0 to 37.5, preferably 5.0 to 13.8, parts by weight of Al_2O_3 and possibly 1.2 to 7.5, in particular 2.4 to 5.0, parts by weight of an oxide of Mn, Mo, V, Zr and/or of an alkaline earth metal.



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13. The catalyst as claimed in claim 11 or 12, which contains Mn oxide or Ba oxide.

14. The catalyst as claimed in one or more of claims 11 to 13, wherein it contains, per 100 parts by weight of Cu, 2.4 to 100, in particular 4.8 to 75, preferably 6 to 44, parts by weight of a support which is insoluble in water, in particular SiO_2, kieselguhr, silica gel, Al_2O_3, preferably Al_2O_3.

15. A process for the preparation of a catalyst as claimed in one or more of claims 1 to 14, wherein an aqueous solution containing salts of copper, zinc, aluminum and possibly of manganese, molybdenum, vanadium, zirconium and/or of an alkaline earth metal, and an aqueous solution of a basic precipitant are separately, but simultaneously, brought together and the precipitation, possibly in the presence of a support, is carried out at a constant pH within a range of 7.0 to 8.5, in particular 7.2 to 8.0, preferably 7.5 to 7.8 and above 70°C, in particular 70 to 95°C, preferably 75 to 85°C, the coprecipitate produced is separated off, washed with water, dried, calcined and reduced if required.

16. The process for the preparation of the catalyst as claimed in claim 15, wherein the calcined catalyst is reduced at 130 to 190°C, possibly under elevated pressure, with a hydrogen/nitrogen mixture, which contains 1.0 to 5% by volume of hydrogen.

17. The use of the catalyst for the hydrogenation of aldehydes to give alcohols.

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