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Copper catalyst

- The invention relates to a novel catalyst which in addition to copper oxide comprises zinc oxide and aluminum oxide, and to a process for the preparation thereof. Because of its high activity and selectivity, the catalyst has proven useful in the hydrogenation of organic compounds, in particular in the hydrogenation of unsaturated or saturated aldehydes, ketones, carboxylic acids or carboxylic esters to form saturated alcohols.
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- 10 Copper-containing catalysts have wide application in chemical technology. Depending on the specific use to which they are put, they differ primarily in the materials which they contain and, if these are the same, in the quantitative composition.
- 15 Specifically, copper oxide/zinc oxide/aluminum oxide catalysts are the basis of the modern processes for synthesizing methanol from carbon monoxide and hydrogen at low pressures.
- For instance, DE-A-2 056 612 describes catalysts for preparing methanol which are compounds of the mix-crystal series $(\text{Cu}_x\text{Zn}_y)\text{Al}_2(\text{OH})_6\text{CO}_3 \cdot 4\text{H}_2\text{O}$, where x and y can take values of from 0.5 to 5.5 and the sum of x and y is 6. The desired mixed crystals are obtained by reaction of aqueous solutions containing copper nitrate, zinc nitrate and aluminum nitrate with basic reagents such as aqueous sodium carbonate solution at pH values between 4.5 and 5.5.
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- 25
- 30 EP-A-0 125 689 likewise relates to copper oxide/zinc oxide/aluminum oxide catalysts for methanol synthesis. They are characterized by a Cu/Zn atom ratio of from 2.8 to 3.8 and an Al_2O_3 content of from 8 to 12 % by weight. They are prepared by coprecipitating copper and zinc with alkaline materials such as an alkali metal or ammonium carbonate in the presence of the aluminum oxide

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component, preferably colloiddally dispersed aluminum oxide or hydroxide, from their aqueous solution. In the unreduced catalyst from 20 to 40% of the pores have a radius of from 1.0 to 3.75 nm and from 60 to 80% of the pores have a radius greater than 3.75 nm.

A further application area for catalysts of the stated material composition is for hydrogenating organic compounds. For this type of reaction $\text{CuO/ZnO/Al}_2\text{O}_3$ catalysts replace copper/chromium oxide catalysts (known as Adkins catalysts), the use of which has been avoided in recent times for ecological reasons, and they are in competition with the multiplicity of nickel catalysts which have been described and introduced to industry.

Hydrogenation catalysts based on copper oxide, zinc oxide and aluminum oxide whose pore volume is made up to the extent of at least approximately 80% by pores having a diameter greater than about 80 Å (8 nm) are the subject of EP 04 24 061. In preferred embodiments the catalyst powder has a surface area of at least 70 m²/g, the average particle diameter is from about 8 to about 28 µm and the atom ratio of copper to zinc is from about 0.2 to about 5.5. The catalysts are produced by preparing two aqueous solutions, one containing copper and zinc salts and the other containing a basic aluminum salt (for example sodium aluminate) and a basic precipitation reagent (for example soda). The two solutions are mixed at the same time with one another in such a ratio that the pH of the resulting mixture is at least about 7. The precipitated solid is subsequently filtered off and calcined. The catalyst is used for hydrogenating aldehydes, ketones, carboxylic acids and carboxylic esters.

The known catalysts containing copper oxide, zinc oxide and aluminum oxide have frequently been developed specifically for particular reactions, for example methanol synthesis or the hydrogenation of organic



compounds. They can nevertheless be used for other chemical reactions, but then do not always produce optimal results. Even different ways of carrying out the same reaction may require the provision of individualized catalysts. Experience has shown that the reaction of the same reactants under different conditions, for example in gaseous or in liquid form on fixed catalysts or on a catalyst suspended in the substrate, requires specially adapted catalysts. In this context it must be remembered that in processes which are carried out on a large scale an increase in conversion or an improvement in the selectivity in the order of even a few tenths of a percent can lead to significant economic advantages.

It is therefore an object of the present invention to prepare catalysts of high activity which can either be used very widely or be targeted at particular processes or process variants.

This object is achieved by a catalyst comprising per 100 parts by weight of copper oxide from 40 to 130 parts by weight of zinc oxide, from 2 to 50 parts by weight of aluminum oxide and from 1 to 4 parts by weight of sodium oxide and having a total surface area (by BET) of from 50 to 100 m²/g, in which from 75 to 95% of the total surface area is made up by pores having radii of from 9 to 1000 nm and the remainder of the total surface area is made up by pores having a radius of less than 9 nm.

The catalyst of the invention has, in comparison with other catalysts of the same or similar qualitative composition, appreciably higher activity and selectivity. It has proven particularly useful as a hydrogenation catalyst and is used very successfully, for example, in the hydrogenation of saturated or unsaturated aldehydes, carboxylic acids or carboxylic esters to form saturated alcohols.

Preferably the catalyst comprised per 100 parts by weight



of copper oxide from 40 to 100, in particular from 45 to 80, parts by weight of zinc oxide, from 4 to 30, in particular from 4 to 20, parts by weight of aluminum oxide and from 1.5 to 3 parts by weight of sodium oxide.

5 The catalyst may optionally contain further metals such as manganese, molybdenum, vanadium, zirconium and/or an alkaline earth metal. Calculated as oxides, namely MnO , MoO_3 , V_2O_5 , ZrO_2 and MeO (Me is an alkaline earth metal), the proportion thereof is per 100 parts by weight of CuO

10 from 0.5 to 8, preferably from 1 to 6, in particular from 2 to 4 parts by weight. The above amounts given for the metal oxides are only for the analytical description of the catalyst. They do not however give the materials of which it is composed in the sense of, for example, sodium

15 actually being present as Na_2O and aluminum being present in the form of the chemical compound Al_2O_3 .

In addition to the materials of which it is composed, the novel catalyst is characterized by the total surface area. This is determined by adsorption of nitrogen in the

20 BET method. The catalyst of the invention in the calcined state, i.e. after heating for from 3 to 10 hours at from 350 to 480°C, preferably from 400 to 460°C, has a surface area of from 50 to 100 m^2/g , in particular from 60 to 80 m^2/g .

25 The novel catalyst is further characterized by a particular pore structure. The proportion of pores having a radius of from 9 to 1000 nm makes up from 75 to 95% of the total surface area, the remainder of the total surface area being made up by pores having a radius of

30 less than 9 nm. Preferably the proportion of pores having a radius of from 9 to 1000 nm is from 80 to 90% and the proportion of pores having a radius of less than 9 nm is from 10 to 20%. Particularly useful are catalysts whose total surface area is made up to the extent of from 55 to

35 85% by pores having a radius of from 15 to 1000 nm, to the extent of from 5 to 25% by pores having a radius of from 9 to less than 15 nm and to the extent of from 10 to



20% by pores smaller than 9 nm. The above pore sizes also relate to the calcined catalyst.

The pore-radius distribution is determined by two methods which supplement one another's areas of application. The distribution of small radii up to a size of about 30 nm is determined by evaluation of the N₂ desorption isotherm by means of the Kelvin equation as in C. Pierce, J. Phys. Chem. 57 (1953), 149 ff. Pore radii of from about 4 nm to about 0.1 mm are determined by mercury penetration as in H.L. Ritter and L.C. Drake, Ind. Eng. Chem. analyt. Ed. 17 (1945), 782.

Pores of the above size and size distribution can be achieved by a high CO₂-content (in the form of carbonate) in the catalyst precursor, i.e. in the product dried at from 50 to 95°C but not yet calcined. It has proven advantageous for this precursor to contain per 100 parts by weight of copper oxide from 32 to 45, preferably from 36 to 40, parts by weight of CO₂.

The novel catalyst can basically be prepared by customary processes, for example, by precipitation of the components from aqueous solution under conditions which ensure the high CO₂-content recognized as advantageous in the catalyst precursor. A particularly suitable process comprises forming an aluminum hydroxide suspension by reaction of an aluminum salt solution with an alkali metal carbonate or alkali metal hydrogen carbonate solution, simultaneously but separately adding at from 80 to 100°C while stirring a solution containing copper and zinc salts and a solution of alkali metal carbonate or alkali metal hydrogen carbonate, filtering off the solid, washing, drying at from 50 to 95°C and then calcining at from 350 to 480°C. The aluminum, copper and zinc salts used are compounds readily soluble in water which are derived from inorganic or even organic acids, such as halides, sulfates or acetates. Because of their high solubility, their chemical inertness and the comparative



ease of removal of the anion and their general availability, nitrates are preferred. Precipitants used are alkali metal carbonates and/or hydrogen carbonates, in particular the sodium salts. The concentration of the salts in the solutions may cover a wide range. The aluminum salt solution contains per liter of solution the aluminum salt in an amount which corresponds to from 20 to 100, preferably from 30 to 90 and in particular from 40 to 80 g of Al_2O_3 . The concentrations of copper and zinc in their joint solution are from 10 to 100 g of Cu and from 5 to 80 g of Zn per liter of solution. The preferred precipitant, sodium carbonate, is advantageously used in the form of a solution which contains from 50 to 150 g of Na_2CO_3 per liter, lower sodium carbonate concentrations not being excluded.

The aluminum hydroxide is precipitated by running an aluminum salt solution at a temperature of from 20 to 90°C over a period of from 2 to 10 minutes into an alkali metal carbonate and/or alkali metal hydrogen carbonate solution having a temperature of from 20 to 100°C, preferably from 30 to 80°C, while stirring vigorously. The ratio of aluminum salt to precipitant is selected so that the pH of the suspension is from 6.5 to 8.5 after the reaction is complete. Subsequently the temperature is adjusted to from 80 to 100°C, preferably from 90 to 98°C, and the alkali metal carbonate and/or alkali metal hydrogen carbonate solution and the copper salt/zinc salt solution, each heated to from 80 to 100°C, preferably from 90 to 98°C, are added simultaneously but separately over a period of from 10 to 30 minutes while stirring vigorously. The rates of addition of the two solutions are mutually adjusted so that the pH of the precipitation suspension remains constant within the range from 7.5 to 8.0. As soon as the addition of the two solutions is complete the suspension is filtered. The filter residue is washed, dried at from 50 to 95°C and subsequently calcined at from 350 to 480°C, preferably at from 400 to 460°C. The shaping of the material, for example by



extrusion or tableting, can be carried out before drying or after calcination. The catalyst is activated by reduction at from 130 to 200°C, preferably at from 150 to 180°C. The reduction is conducted in a separate reactor or directly in the hydrogenation reactor.

The novel catalyst is successfully used for hydrogenating organic compounds, preferably for hydrogenating unsaturated or saturated aldehydes, ketones, carboxylic acids or carboxylic esters. It has proven particularly useful in the hydrogenation of unsaturated and saturated aldehydes in the gas phase.

The examples below illustrate the invention without limiting it in any way.

Example 1: Catalyst preparation

A solution at room temperature of 925 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 3 l of water is run into a solution heated to 70°C of 580 g of soda in 5.5 l of water while stirring vigorously. While continuing stirring the temperature of the suspension obtained is raised to 95°C over a period of about 10 minutes and a solution heated to 95°C of 2249.2 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 1755.4 g of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 10 l of water and a solution likewise heated to 95°C of 2340 g of Na_2CO_3 in 18 l of water were added simultaneously but separately over a period of 15 minutes. During the reaction the precipitation suspension is maintained at a pH of from 7.5 to 8.0. Subsequently the suspension is stirred for a further 2 minutes and then filtered. The filter residue is continuously washed for 80 minutes with 80 l of water and after shaping by extrusion or by spray drying is dried at no more than 100°C to a water content of less than 5%.

The dried uncalcined catalyst precursor comprises 38.8 % by weight of CuO (31 % by weight Cu), and 65 parts by weight of ZnO, 17 parts by weight of Al_2O_3 , 2.0 parts by



weight of Na_2O and 38.6 parts by weight of CO_2 per 100 parts by weight of CuO .

5 In a subsequent process step the precursor is heated in a stream of nitrogen or air (200 l/h) to 430°C and maintained at this temperature for a further 3 hours. The resulting calcined product comprises 51 % by weight of CuO , and 65 parts by weight of ZnO , 17 parts by weight of Al_2O_3 , 2.0 parts by weight of Na_2O and 1.5 parts by weight of CO_2 per 100 parts by weight of CuO . It has a total
10 surface area (by BET) of $68 \text{ m}^2/\text{g}$; 85% of the surface area is made up by pores having radii greater than 9 nm and 16% is made up by pores having radii less than 9 nm.

The calcined product can be used in extruded or tableted form as a fixed-bed catalyst.

15 Example 2: Hydrogenation of n-butyraldehyde

250 ml of the catalyst prepared as in Example 1 and tableted are reduced in a reaction tube at 160°C with 400 l/h of a H_2/N_2 mixture containing 3 % by volume of H_2 until no more water is formed. Subsequently a mixture of
20 250 ml of gaseous n-butyraldehyde and 710 l of hydrogen per hour are passed over the catalyst at 145°C and a gauge pressure of 0.3 MPa. The excess hydrogen is recirculated.

25 The hydrogenation product has the following composition determined by gas chromatography:

	n-butanol	99.8 % by weight
	n-butyraldehyde	< 0.05 % by weight
	butyl butyrate	< 0.05 % by weight
	2-ethylhexanol	< 0.05 % by weight
30	di-n-butyl ether	≤ 10.0 % by weight

Particularly noteworthy in comparison with the prior art is the exceptionally low formation of byproducts when



using the catalysts of the invention.

Example 3: Hydrogenation of 2-ethylhexenal

3 l of the catalyst prepared as in Example 1 and tableted
are reduced as described in Example 2. Subsequently a
5 gaseous mixture of 1500 ml/h of 2-ethylhexenal (liquid)
and 4.4 standard m³/h of hydrogen is passed over it at
145°C and a gauge pressure of 50 kPa. Starting material
and reaction product have the following composition
determined by gas chromatography:

10		Starting material (% by weight)	Reaction product (% by weight)
	C ₇ /C ₈ hydrocarbons	≤ 0.1	≤ 0.1
	n/i-butanal	3 - 4	-
15	n/i-butanol	0.5 - 1.5	3.5 - 4.5
	2-ethylhexenal	90 - 91.5	≤ 0.1
	2-ethylhexanal	about 1	0.2 - 0.3
	2-ethylhexanol	3.5 - 4.5	95 - 97
20	higher boiling-point components (such as acetals, diols)	2 - 3	0.5 - 0.8

Example 4 (comparative): Hydrogenation of n-butyraldehyde

In this example a catalyst of the prior art is used. It
comprises 47.5 % by weight of Cu, and 49.5 parts by
25 weight of ZnO, 8.4 parts by weight of Al₂O₃, and 0.12 parts
by weight of Na₂O per 100 parts by weight of CuO. Its
total surface area (by BET) is 128 g/m²; 85% of the
surface area is made up by pores having a radius less
than or equal to 15 nm.

30 250 ml of the tableted catalyst are reduced in a tube
reactor, as described in Example 2. Subsequently a
gaseous mixture of 250 ml/h of n-butyraldehyde (liquid)
and 710 l of hydrogen per hour is passed over the



catalyst at 145°C and a gauge pressure of 0.3 MPa. The excess hydrogen is recirculated.

The hydrogenation product has the following composition by gas chromatography:

5	n-butanol	99.5 - 99.6 % by weight
	n-butyraldehyde	0.2 - 0.3 % by weight
	butyl butyrate	about 0.02 % by weight
	di-n-butyl ether	about 100 ppm by weight

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WHAT IS CLAIMED IS:

1. A catalyst comprising per 100 parts by weight of copper oxide from 40 to 130 parts by weight of zinc oxide, from 2 to 50 parts by weight of aluminum oxide and from 1 to 4 parts by weight of sodium oxide and having a total surface area (by BET) of from 50 to 100 m²/g, in which from 75 to 95% of the total surface area is made up by pores having radii of from 9 to 1000 nm and the remainder of the total surface area is made up by pores having a radius of less than 9 nm.
2. A catalyst as claimed in claim 1, comprising per 100 parts by weight of copper oxide from 40 to 100, in particular from 45 to 80, parts by weight of zinc oxide, from 4 to 30, in particular from 4 to 20, parts by weight of aluminum oxide and from 1.5 to 3 parts by weight of sodium oxide.
3. A catalyst as claimed in claim 1 or 2, comprising per 100 parts by weight of copper oxide from 0.5 to 8 parts by weight of manganese, molybdenum, vanadium, zirconium and/or an alkaline earth metal (calculated as MnO, MoO₃, V₂O₅, ZrO₂, MeO, Me = alkaline earth metal).
4. A catalyst as claimed in claim 3, comprising from 1 to 6, in particular from 2 to 4, parts by weight of the metals manganese, molybdenum, vanadium, zirconium and/or an alkaline earth metal (calculated as MnO, MoO₃, V₂O₅, ZrO₂, MeO, Me = alkaline earth metal).
5. A catalyst as claimed in one or more of claims 1 to 4, having a surface area of from 60 to 80 m²/g (by BET).
6. A catalyst as claimed in one or more of claims 1 to

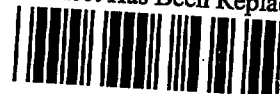




5, wherein from 80 to 90% of the total surface area is made up by pores having a radius of from 9 to 1000 nm and from 10 to 20 % of the total surface area is made up by pores having a radius less than 9 nm.

- 5 7. A catalyst as claimed in one or more of claims 1 to 6, wherein from 55 to 85% of the total surface area is made up by pores having a radius of from 15 to 1000 nm, from 5 to 25% of the total surface area is made up by pores having a radius of from 9 to less than 15 nm and from 10 to 20% of the total surface area is made up by pores having a radius less than 9 nm.
- 10 8. A process for preparing a catalyst as claimed in one or more of claims 1 to 7, which comprises forming an aluminum hydroxide suspension by reaction of an aluminum salt solution with an alkali metal carbonate and/or alkali metal hydrogen carbonate solution, simultaneously but separately adding while stirring a solution heated to from 80 to 100°C containing
15 copper and zinc salts and a solution heated to from 80 to 100°C of alkali metal carbonate or alkali metal hydrogen carbonate while maintaining a pH of 7.5 to 8.0 in the precipitation suspension, filtering off the solid, washing, drying at from 50 to 95°C and then calcining at from 350 to 480°C.
- 20 9. The process as claimed in claim 8, wherein the aluminum hydroxide suspension is prepared by adding an aluminum salt solution having a temperature of from 20 to 90°C while stirring vigorously to an alkali metal carbonate and/or hydrogen carbonate solution having a temperature of from 20 to 100°C in such an amount that after completion of the reaction the pH
25 of the suspension is from 6.5 to 8.5.
10. A method of using the catalyst as claimed in one or more of claims 1 to 7 for hydrogenating organic

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compounds, in particular for hydrogenating unsaturated or saturated aldehydes, ketones, carboxylic acids or carboxylic esters to form saturated alcohols.

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