

O.Z. 0050/43816

Catalysts with fine-particle dispersion
of the active component

The present invention relates to catalysts with fine-particle dispersion of the active component and to
5 a process for preparing these catalysts.

WO-A-89/00082 and the citations given therein describe the preparation of oxide catalysts which contain Cu, Zn and Al, employing as precursor a Cu-An-Al alloy which is partly or completely converted into the oxide in
10 an oxidation step. The catalysts are employed for preparing methanol.

DE-A-37 17 111 discloses a process for preparing a copper-containing catalyst for low-temperature shift conversion which, besides copper oxide, also [lacuna]
15 zinc oxide and aluminum oxide. The catalyst is prepared by precipitation of the water-soluble salts from aqueous solution using an alkaline precipitant.

The known catalysts are unsatisfactory in respect of useful life and activity.

20 It is an object of the present invention to remedy the abovementioned disadvantages.

We have found that this object is achieved by novel and improved catalysts prepared by combining $M-Al_2O_4$ where M is an element of Group Ib, VIIb or VIII
25 of the Periodic Table of the Elements with tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements as oxide or salt or in elemental form and calcining at 300-1300°C under 0.1-200 bar.

The catalysts according to the invention can be
30 prepared as follows:

The starting material may be a solid oxide which is wholly or partly, ie. 1-100%, preferably 10-90%, particularly preferably 20-70%, by weight, a spinel of the composition $M-Al_2O_4$ in an Al_2O_3 matrix, and this can
35 be mixed with the same or higher concentration of tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements, as oxide or salt or in elemental

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form, and calcined at 300-1300°C, preferably 500-1200°C, particularly preferably 600-1100°C, under 0.1-200 bar, preferably 0.5-10 bar, particularly preferably under atmospheric pressure.

- 5 The mixing can take place, for example, by spraying, mechanical mixing, stirring or kneading the ground solid of the composition $M-Al_2O_4$, preferably in Al_2O_3 , particularly preferably in $\gamma-Al_2O_3$, or preferably by impregnating an unground solid of the composition
- 10 $M-Al_2O_4$, preferably in Al_2O_3 , particularly preferably in $\gamma-Al_2O_3$, with a solution of salts of tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements.

- The liberation of the element M in the form of
- 15 the element or oxide, which as a rule leads to fine-particle dispersion, can be induced by replacing the element M in the spinel in the calcination step by tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements, in the form of the element, oxide
- 20 or salt-like compound when the resulting spinel is more thermodynamically stable than the original spinel $M-Al_2O_4$.

- Suitable as metal M in the starting oxides $M-Al_2O_4$ are elements of group Ib, VIIb and VIII of the
- 25 Periodic Table of the Elements in the +2 oxidation state, such as Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} , especially Ni^{2+} and Cu^{2+} or mixtures thereof.

- The elements of group IIa or IIb of the Periodic Table of the Elements can be used in the form of the
- 30 metal, oxides or salt-like compounds. Examples of salt-like compounds are carbonates, hydroxides, carboxylates, halides and oxo anions such as nitrates, nitrites, sulfites, sulfates, phosphites, phosphates, pyrophosphates, halites, halates and basic carbonates, preferably
- 35 carbonates, hydroxides, carboxylates, nitrates, nitrites, sulfates, phosphates and basic carbonates, particularly preferably carbonates, hydroxides, basic carbonates and



nitrates, preferably in the +2 oxidation state such as Zn^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} , especially Zn^{2+} and Mg^{2+} or mixtures thereof.

The preparation of the starting oxide of the composition $\text{M-Al}_2\text{O}_3$, preferably in the form of a spinel, is disclosed in, for example, WO-A-82/00820, SU-A-426 968, FR-A-2 655 878 and Rev. Chim. 20 (1969) 105-106. It proves advantageous to impregnate an Al_2O_3 carrier with a soluble compound such as a salt of the cation M, eg. a nitrite, nitrate, sulfite, sulfate, carbonate, hydroxide, carboxylate, halide, halite or halate, and subsequently to decompose the anion to the oxide thermally. Another possibility comprises mixing a compound such as a salt of the cation R [sic] with an oxygen-containing aluminum compound, eg. by drying or in suspension, especially by spray-drying, compacting the material, eg. by kneading, where appropriate by adding a suitable molding aid, molding by extrusion, drying and subsequently calcining to form the spinel. The calcination can be carried out at 300-1300°C, preferably 600-1000°C.

Doping of aluminum oxide carriers with a large surface area, ie. the formation of mixed oxides, increases the thermal stability of the carrier (eg. DE-A-34 03 328, DE-A-25 00 548, Appl. Catal. 7 (1983) 211-220, J. Catal. 127 (1991) 595-604). The foreign ions may additionally contribute to the catalytic activity of the catalyst. The following elements may be generally employed for the doping: alkali metals, rare earth metals, Sc, Ti, V, Cr, Y, Zr, B, Si, Ge, P, Bi. The degree of replacement of aluminum oxide can be, for example, 0.01-20% by weight.

The particle size of the oxide of the metal M in the unused catalyst is 1-200 nm, preferably 3-100 nm, particularly preferably 10-50 nm. The particle size can be determined, for example, by XRD (X-ray diffraction [sic]) or TEM (transmission electron microscopy).



The catalysts according to the invention contain mesopores of 2-20 nm and macropores of more than 20 nm and [lacuna] BET surface areas of 1-350 m²/g, preferably 10-200 m²/g, particularly preferably 25-150 m²/g, and 5 porosity of 0.01-0.8 ml/g.

The catalysts according to the invention are suitable, for example, for CO conversion and for methanol synthesis.

EXAMPLES

10 Preparation of the catalyst

EXAMPLE 1

A mixture of 284 g of Puralox[®] SCF (from Condea), 166 g of Pural[®] SB (from Condea) and 100 g of CuO (from Merck) was kneaded with 20 ml of formic acid (dissolved 15 in 140 ml of H₂O) for 0.75 h, extruded to 3 mm extrudates, dried and calcined at 800°C for 4 h.

A CuAl₂O₄-containing solid with a BET surface area of 112 m²/g and a bimodal pore radius distribution with the diameter of 25% of the pores being in the range 20 10-1 micrometers and of 65% of the pores being in the range 20-5 nanometers was obtained.

71.4 g of the CuAl₂O₄-containing solid (water uptake: 69.1%) were impregnated twice with 49 ml of an aqueous solution which contained nitric acid (pH 3) and 25 32.6 g of Zn(NO₃)₂ and then left at room temperature for one hour. The impregnated carrier was dried to constant weight at 120°C and finally calcined at 600°C for 4 h.

A ZnAl₂O₄-containing solid with a BET surface area of 82 m²/g and an unchanged bimodal pore radius 30 distribution was obtained with formation of CuO.

The size of the copper oxide crystallites was determined using X-rays and is 28 nm.





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We claim:

1. A catalyst prepared by combining $M-Al_2O_4$ where M is an element of Group Ib, VIIb or VIII of the Periodic Table of the Elements with tin, lead, an element of group
5 IIa or IIb of the Periodic Table of the Elements as oxide or salt or in elemental form and calcining at 300-1300°C under 0.1-200 bar.
2. A process for preparing catalysts, which comprises combining oxides of the formula $M-Al_2O_4$ where M is
10 an element of Group Ib, VIIb or VIII of the Periodic Table of the Elements with tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements as oxide or salt or in elemental form and calcining at 300-1300°C under 0.1-200 bar.
- 15 3. A process for preparing catalysts as claimed in claim 2, wherein the substituent M in the oxides $M-Al_2O_4$ is an element of Group Ib, VIIb or VIII of the Periodic Table of the Elements.
4. A process for preparing catalysts as claimed in
20 claim 2, wherein zinc, magnesium, calcium, strontium or barium is used as oxide or salt or in elemental form.
5. A process for preparing catalysts as claimed in claim 2, wherein the compounds of Group Ib, VIIb and VIII of the Periodic Table of the Elements are oxides of
25 manganese, iron, cobalt, nickel or copper.

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Abstract of the Disclosure: Catalysts prepared by combining $M-Al_2O_3$ where M is an element of Group Ib, VIIb or VIII of the Periodic Table of the Elements with tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements as oxide or salt or in elemental form and calcining at 300-1300°C under 0.1-200 bar and the process for preparing them.

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DE-A-37 17 111 discloses a process for preparing a copper-containing catalyst for low-temperature shift conversion which, besides copper oxide, also contains zinc oxide and aluminum oxide. The catalyst is prepared by precipitation of the water-soluble salts from aqueous solution using an alkaline precipitant.

The known catalysts are unsatisfactory in respect of useful life and activity.

It is an object of the present invention to remedy the abovementioned disadvantages.

We have found that this object is achieved by novel and improved catalysts prepared by combining $M-Al_2O_3$, where M is an element of Group Ib, VIIb or VIII of the Periodic Table of the Elements with tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements as oxide or salt or in elemental form and calcining at 300-1300°C under 0.1-200 bar.

The catalysts according to the invention can be prepared as follows:

The starting material may be a solid oxide which is wholly or partly, ie. 1-100%, preferably 10-90%, particularly preferably 20-70%, by weight, a spinel of the composition $M-Al_2O_3$ in an Al_2O_3 matrix, and this can be mixed with the same or higher concentration of tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements, as oxide or salt or in elemental form, and

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calcined at 300-1300°C, preferably 500-1200°C, particularly preferably 600-1100°C, under 0.1-200 bar, preferably 0.5-10 bar, particularly preferably under atmospheric pressure.

The mixing can take place, for example, by spraying, mechanical mixing, stirring or kneading the ground solid of the composition $M-Al_2O_4$, preferably in Al_2O_3 , particularly preferably in $\gamma-Al_2O_3$, or preferably by impregnating an unground solid of the composition $M-Al_2O_4$, preferably in Al_2O_3 , particularly preferably in $\gamma-Al_2O_3$, with a solution of salts of tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements.

The liberation of the element M in the form of the element or oxide, which as a rule leads to fine-particle dispersion, can be induced by replacing the element M in the spinel in the calcination step by tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements, in the form of the element, oxide or salt-like compound when the resulting spinel is more thermodynamically stable than the original spinel $M-Al_2O_4$.

Suitable as metal M in the starting oxides $M-Al_2O_4$ are elements of group Ib, VIIb and VIII of the Periodic Table of the Elements in the +2 oxidation state, such as Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} , especially Ni^{2+} and Cu^{2+} or mixtures thereof.

The elements of group IIa or IIb of the Periodic Table of the Elements can be used in the form of the metal, oxides or salt-like compounds. Examples of salt-like compounds are carbonates, hydroxides, carboxylates, halides and oxo anions such as nitrates, nitrites, sulfites, sulfates, phosphites, phosphates, pyrophosphates, halites, halates and basic carbonates, preferably carbonates, hydroxides, carboxylates, nitrates, nitrites, sulfates, phosphates and basic carbonates, particularly preferably carbonates, hydroxides, basic carbonates and nitrates, preferably in the +2 oxidation state such as Zn^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} and Ba^{2+} , especially Zn^{2+} and Mg^{2+} or

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4. A process for preparing catalysts as claimed in claim 2, wherein zinc, magnesium, calcium, strontium or barium is used as oxide or salt or in elemental form.
5. A process for preparing catalysts as claimed in claim 2, wherein the compounds of the elements of Group Ib, VIIb and VIII of the Periodic Table of the Elements are oxides of manganese, iron, cobalt, nickel or copper.

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CATALYSTS WITH FINE-PARTICLE DISPERSION
OF THE ACTIVE COMPONENT

Abstract of the Disclosure: Catalysts prepared by combining $M-Al_2O_3$, where M is an element of Group Ib, VIIb or VIII of the Periodic Table of the Elements with tin, lead, an element of group IIa or IIb of the Periodic Table of the Elements as oxide or salt or in elemental form and calcining at 300-1300°C under 0.1-200 bar and the process for preparing them.

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CATALYSTS WITH HIGHLY DISPERSED ACTIVE COMPONENTS

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