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Process for reducing oxidic hydrogenation catalysts

The invention relates to a process for reducing oxidic hydrogenation catalysts and a process for hydrogenating aldehydes over the reduced catalysts to
5 form alcohols.

The invention also relates to the use of the alcohols prepared in this way.

10 Alcohols can be prepared by catalytic hydrogenation of aldehydes which, for example, have been obtained by hydroformylation of olefins or by aldol condensation. Large amounts of alcohols are used as solvents and as intermediates for the preparation of many organic compounds. Important downstream products of alcohols are plasticizers and detergents.

15 It is known that aldehydes can be reduced catalytically with hydrogen to form alcohols. Here, use is frequently made of catalysts which comprise at least one metal from groups 1b, 2b, 6b, 7b and/or 8 of the Periodic Table of the Elements. The hydrogenation of aldehydes can be carried out continuously or batchwise in the gas or liquid phase using pulverulent or shaped catalysts.
20 For the industrial preparation of alcohols by hydrogenation of aldehydes, preference is given, especially in the case of high-volume products, to continuous processes using fixed-bed catalysts in the gas or liquid phase. Compared to gas-phase hydrogenation, the liquid-phase hydrogenation has the more favorable energy balance. This advantage increases with increasing
25 molar mass of the aldehyde to be hydrogenated. Higher aldehydes having more than 7 carbon atoms are therefore preferably hydrogenated in the liquid phase.

The industrially customary hydrogenation catalysts are produced by reduction
30 of appropriate precursors which contain the catalytically active metals in oxidic or salt-like form. Hydrogenation catalysts which have been activated in this way are very reactive and are rapidly oxidized in air; some are even pyrophoric.

35 The reduction of the catalyst precursors should, in order to keep the startup times or downtimes of a hydrogenation reactor as short as possible, occur as



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quickly as possible but without impairing the activity and/or operating life of the catalyst.

The reduction of catalyst precursors arranged in a fixed bed to give the actual active metal-containing catalyst species is a step which has a critical influence on the success of the subsequent hydrogenation process. During the reduction of the metal compounds present in the catalyst precursor, heat is liberated. This amounts, for example, to 20 kcal/mol in the reduction of CuO to Cu. Overheating of the precursor or the catalyst during the reduction has to be prevented because otherwise thermal damage to the catalyst, e.g. enlargement of the metal crystallites, occurs. In order to obtain a hydrogenation catalyst having an optimum activity and a high strength, the reduction has to be carried out under extremely careful temperature control.

The reduction of catalyst precursors can be carried out in the presence of a liquid phase or a gas mixture.

In the absence of a liquid phase, the catalyst precursor is frequently reduced using a gas mixture consisting of hydrogen and an inert gas, preferably nitrogen. Thus, the gas-phase reduction of a copper catalyst is described in JP 61-161146. Reduction of Cu/Zn catalysts is known from DE 17 68 313 and DE 34 43 277. JP 1-127042 discloses the gas-phase reduction of Cu/Cr catalysts.

Owing to the low heat capacity of gas mixtures, the reduction can be carried out only slowly and/or a very high gas hourly space velocity (GHSV) has to be set to ensure removal of heat. The reduction using a high gas hourly space velocity produces large amounts of gas which have to be disposed of. Owing to its high inert gas content, working up the gas to recover hydrogen is not worthwhile. The high gas hourly space velocity can be achieved more economically by circulating the gas with the aid of a circulating gas blower.

As an alternative to the gas-phase reduction, the catalyst precursor can be reduced in the presence of a liquid phase. Here, the heat of reduction is removed by means of the liquid. According to GB 385 625, a Cu/Cr catalyst precursor is reduced in the presence of a carboxylic ester at a liquid hourly space velocity (LHSV) of 8 h⁻¹. JP 47-14113 describes the activation of a

Cu/Cr catalyst in a stream of lactone ($LHSV = 0.67 \text{ h}^{-1}$) at 200°C . A further method of reducing Ni/Cu/Mo or Co/Cu catalyst precursors is disclosed in DE 35 24 330. Here, the reduction is carried out at 200°C and 250 bar in a stream of isopropanol at a throughput per unit cross-sectional area of
5 $60 \text{ m}^3/(\text{m}^2 \cdot \text{h})$ for an Mo-containing catalyst and of $30 \text{ m}^3/(\text{m}^2 \cdot \text{h})$ for a Co-containing catalyst.

These reduction processes have the disadvantage that they employ high temperature and/or pressures and require long reaction times up to a number
10 of days.

A further process for reducing hydrogenation catalysts is described in EP 0 689 477. Here, copper-containing catalyst precursors, in particular Cu/Cr, Cu/Zn, Cu/Fe, Cu/Al and Cu/SiO₂ catalyst precursors, are reduced in the
15 liquid phase in a two-stage process. The liquid phase can comprise esters, alcohols or hydrocarbons.

The two-stage process of EP 0 689 477 employs a temperature program in which at least 10% by weight of the copper is reduced in the first stage at a
20 temperature of from 20 to 140°C . In the second stage, the temperature is increased from 140 to 250°C . Disadvantages are the complicated temperature control and the still long reduction time of, on average, 40 hours.

It is therefore an object of the present invention to provide a process for
25 reducing catalyst precursors by means of which short reduction times can be achieved without the activity of the resulting catalyst being impaired. The reduced catalysts should, in particular, be suitable for preparing alcohols by hydrogenation of the corresponding aldehydes.

30 It has now been found that the reduction of a catalyst precursor can be carried out in a short time in the presence of a solvent at elevated temperature and moderate pressure in a liquid-phase hydrogenation unit without loss of activity and that the resulting catalysts are very suitable for the preparation of alcohols.

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The present invention accordingly provides a process for reducing nickel-containing catalysts for aldehyde hydrogenation, in which the reduction is

carried out in the liquid phase in a single-stage process by means of hydrogen.

5 The process of the invention has a number of advantages: the reduction of the catalyst precursor can be carried out under gentle conditions in a liquid-phase hydrogenation unit, so that optimum activity and strength of the catalyst are obtained. No circulating gas blower is necessary for carrying out the reduction, so that no additional capital costs are incurred. The reduction can be carried out in less than 24 hours, which significantly shortens the
10 downtime of the hydrogenation plant when changing the catalyst compared to other reduction processes. The catalyst is formed in the low pressure range from 1 to 25 bar, so that no additional high-pressure resistant vessels or reactors are necessary.

15 A single-stage reduction in the sense of the present invention employs fixed reaction parameters. Thus, pressure and temperature are fixed and not changed anymore. Heat can be supplied, for example, by means of an appropriately heated liquid phase. The reduction is carried out by means of hydrogen; it is also possible to use hydrogen-containing mixtures. The
20 reduction of the nickel-containing catalysts can be carried out in the same reactor as the subsequent aldehyde hydrogenation.

To hydrogenate aldehydes by means of the process of the invention in the liquid phase, it is possible to use pelletized or shaped, fixed-bed catalysts
25 which are prepared by reduction according to the invention of corresponding precursors. Suitable precursors can comprise the metals of groups 1b, 2b, 6b, 7b and/or 8 of the Periodic Table, in particular nickel, copper and chromium. Catalysts applied to supports or unsupported catalysts can be used. Unsupported catalysts generally comprise from about 0.2 to 30% by weight
30 of nickel, from 25 to 40% by weight of copper and from 18 to 40% by weight of chromium. The catalysts can further comprise up to 20% by weight of basic substances such as alkali metal or alkaline earth metal oxides or hydroxides, and also other inert or property-modifying materials in the same amounts, for example graphite.

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Preferred catalysts in the process of the invention for hydrogenating aldehydes to give alcohols are supported catalysts. They comprise from 0.3

to 15% by weight of copper and from 0.3 to 15% by weight of nickel and also, as activators, from 0.05 to 3.5% by weight of chromium and advantageously from 0.01 to 1.6% by weight of an alkali component on a support material. The support material preferably comprises aluminum oxide or silicon oxide.

- 5 The amounts indicated are based on the unreduced catalyst, i.e. the catalyst precursors.

The catalyst precursors, i.e. the unreduced catalysts, are advantageously used in a form which offers a low resistance for flow, e.g. in the form of
10 granules, pellets or shaped bodies such as tablets, cylinders, extrudates or rings.

According to the invention, the reduction of the catalyst precursor occurs in the presence of a liquid phase which can serve as heat transfer medium. As liquid phase, use is made of liquid organic materials which do not dissolve
15 any component from the catalyst precursor, cause no structural changes in the catalyst, undergo no reactions with the metal components or the support material and do not irreversibly occupy the active sites of the catalyst. Suitable materials are, for example, hydrocarbons, esters, lactones and alcohols which are liquid under the reaction conditions. It is also possible to
20 use solvent mixtures consisting of, for example, hydrocarbons and alcohols or of a plurality of different alcohols. The liquid phase preferably comprises alcohols or alcohol mixtures, particularly preferably alcohols having from 6 to 25 carbon atoms. In a particular embodiment of the invention, the liquid phase comprises alcohols from an aldehyde hydrogenation.

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The aldehydes to be hydrogenated can be prepared by hydroformylation of olefins, e.g. as described in DE 196 54 340.1. The aldehydes can also be prepared by aldol condensation, e.g. of butyraldehydes or valeraldehydes. Examples of aldehydes which can be hydrogenated using the catalysts
30 reduced according to the invention are butyraldehyde, valeraldehyde, hexanal, heptanal, octanals, octenals such as 2-ethylhex-2-enal, isononanals, decanals, decenals or tridecanals.

The liquid phase used preferably comprises the hydrogenation products of
35 these aldehydes (e.g. butanol, 2-ethylhexanol, isononanol, isodecanol or tridecanol).

The reduction time of the catalyst precursors in the process of the invention is generally less than 24 hours and is thus considerably shorter than in known processes. The LHSV of one of the abovementioned liquids over the catalyst precursor can be from 0.1 to 10 h⁻¹, preferably from 1 to 5 h⁻¹. At these space
5 velocities, the liquid flows uniformly around the catalyst precursor. This measure improves heat transfer from the catalyst precursor to the liquid so that local overheating of the catalyst precursor ("hot spots") can be ruled out.

The reducing gas used in the process of the invention comprises inert gas,
10 preferably nitrogen, and hydrogen. The hydrogen content can be increased during the reduction starting from pure inert gas, so that uniform reduction of the catalyst precursor is achieved. The proportion by volume of hydrogen can rise from 0 to 100% by volume; the hydrogen concentration is preferably between 20 and 80% by volume.

15 In the process of the invention, the gas hourly space velocity (GHSV) is from 1 to 50 h⁻¹, preferably from 2 to 10 h⁻¹. The major part of the water of reaction is carried out together with the waste gas.

20 The reduction of the catalyst precursor is preferably carried out at the same pressure as or a lower pressure than the subsequent aldehyde hydrogenation. The pressure is preferably from 1 to 25 bar, i.e. in the low pressure range. When using a liquid phase having a boiling point (at atmospheric pressure) which is higher than the reduction temperature, the
25 reduction is preferably carried out at a pressure of from 1 to 2 bar. If the liquid phase used is a liquid or liquid mixture having a low boiling point (at atmospheric pressure), the pressure has to be increased so that the solvent used is present in liquid form in the reactor and only little of it is lost with the waste gas.

30 The reduction of the catalyst precursor can be carried out in the temperature range from 100 to 200°C, preferably from 130 to 170°C, and a pressure of from 1 to 25 bar, preferably from 1 to 10 bar.

35 The reduction time is dependent on the conditions selected. The course of the reduction is followed by means of the water balance and the reduction time is generally less than 24 hours, preferably from 6 to 18 hours.

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The catalysts obtained in this way are suitable for the hydrogenation of aldehydes or aldehyde mixtures, in particular aldehydes or aldehyde mixtures which have been prepared by hydroformylation of olefins or by aldol condensation.

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The present invention therefore also provides a process for preparing alcohols having from 2 to 20 carbon atoms by hydrogenation of the corresponding aldehydes over nickel-containing catalysts, in which the nickel-containing catalysts are reduced in the liquid phase in a single-stage process
10 by means of hydrogen prior to the hydrogenation of the aldehydes.

Furthermore, the invention provides for the use of the alcohols prepared by the process of the invention as plasticizer alcohols or in detergents.

15 The aldehydes to be hydrogenated can be obtained by hydroformylation of olefins. It is possible to use aldehydes which have already been purified, but the reactor output from the hydroformylation, if appropriate after separating off a catalyst phase, i.e. a mixture of aldehydes, alcohols, olefins and/or high boilers, can also be used in the hydrogenation process of the invention.

20 The aldehydes can, as already indicated, be prepared by hydroformylation of olefins or aldol condensation. The aldehydes and thus the alcohols preferably have from 2 to 20, particularly preferably from 4 to 16, carbon atoms. Very particularly preferred aldehydes are C₄-, C₅-, C₆-, C₈- or C₁₃-aldehydes. The aldehydes can be aliphatically saturated or unsaturated.

25 The reduction according to the invention of α , β -unsaturated aldehydes leads to completely saturated alcohols; thus, 2-ethylhex-2-enal is hydrogenated to 2-ethylhexanol. In the reduction of olefinically unsaturated aldehydes having double bonds which are not conjugated with the aldehyde function, only the aldehyde function is hydrogenated while the olefinic double bonds are largely
30 retained.

In the process of the invention for preparing alcohols by hydrogenation of the corresponding aldehydes over nickel-containing catalysts, the liquid phase used in the reduction of the catalyst can comprise alcohols, preferably ones
35 from the hydrogenation of aldehydes.

If the liquid phase comprises alcohols, these can, of course, be identical to

the alcohols produced by the hydrogenation of the aldehydes.

If, for example, isononanal is hydrogenated to isononanol over the catalyst activated according to the invention, the liquid phase used for the reduction
5 of the catalyst advantageously also comprises isononanol.

The preparation of alcohols according to the invention, i.e. the hydrogenation of aldehydes, can be carried out in the same reactor as the reduction of the nickel-containing catalysts.

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The reduction of the nickel-containing catalysts to be carried out prior to the hydrogenation can be carried out at a temperature of from 100 to 200°C, preferably from 130 to 170°C, and a pressure of from 1 to 25 bar, preferably from 1 to 10 bar.

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For the liquid-phase hydrogenation of the aldehydes or the hydroformylation mixtures, a variety of process variants can be selected. It can be carried out adiabatically or virtually isothermally, i.e. with a temperature rise of < 10°C, in one or two stages. In the latter case, both reactors, advantageously tube
20 reactors, can be operated adiabatically or virtually isothermally or one reactor can be operated adiabatically and the other reactor operated isothermally. Furthermore, it is possible to hydrogenate the aldehyde mixtures in a straight pass or with product recirculation. The reactors can be operated as cocurrent reactors with trickle flow or preferably with high liquid hourly space velocities
25 (pulse flow). The liquid-phase hydrogenation of the invention can be carried out under a total pressure of from 5 to 25 bar, preferably from 15 to 25 bar. If necessary, the hydrogenation mixtures are purified further, e.g. by distillation.

30 The alcohols prepared using the process of the invention can be used as plasticizer alcohols, e.g. in the form of phthalic diesters, or as detergents.

The following examples illustrate the invention but do not restrict its scope.

35 **Example 1 (comparative example)**

10 l of catalyst precursor of a Cu/Cr/Ni-containing supported catalyst were

reduced in the absence of a liquid phase:

Composition of the catalyst precursor:

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86% by weight	Al ₂ O ₃
9% by weight	CuO
4% by weight	NiO
1% by weight	Cr ₂ O ₃

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After introduction of the catalyst precursor, the apparatus was flushed free of oxygen using nitrogen. The apparatus was pressurized with 2 bar of nitrogen, the circulating gas compressor was started up and the apparatus was heated to 150°C. The amount of gas circulated was 3.5 m³/h. During the entire
 15 reduction time, nitrogen was taken off in an amount of 10 l/h of input and output gas under pressure regulation (2 bar). During the course of the reduction, hydrogen was metered in in an increasing amount (see Table 1). The temperature in the contact bed was maintained at 160 ± 5°C.

20 Table 1. Catalyst reduction in the gas phase

Time in hours	Temperature	Hydrogen in standard l/h	Nitrogen in standard l/h
0-8 h	160	2.5	10
9-16 h	161	5.0	10
25 17-24 h	159	7.5	10
25-32 h	160	10.0	10
33-40 h	161	12.5	10
41-48 h	160	15.0	10
49-56 h	161	17.5	10

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The activity of the catalyst which had been reduced in this way was tested in a circulation reactor. For this purpose, one liter of a reaction product from an Rh-catalyzed hydroformylation of tributene was hydrogenated in the liquid phase at 180°C and 25 bar absolute over 100 g of the Cu/Cr/Ni catalyst
 35 prepared as described above (target product: C₁₃-alcohols). The analyses of the starting material and product are shown in Table 2.

Table 2. Activity testing of the catalyst reduced in the gas phase

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	1/LHSV $I_{cat} \cdot h / I_{starting \text{ material}}$	Olefins % by weight	Pa- raffins % by weight	Alde- hydes % by weight	Alco-hols % by weight	High boilers % by weight
Starting material	0	14.8	1.2	76.5	4.5	3.0
Product	1.75	14.3	1.7	0.3	80.4	3.3

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Example 2

10 l of the catalyst precursor from Example 1 were reduced as follows in the presence of a liquid phase:

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The liquid phase used was isotridecanol which had been obtained by Rh-catalyzed hydroformylation of tributene and subsequent hydrogenation. Isotridecanol was pumped by means of a circulation pump via a heat exchanger for setting the temperature and through the reactor charged with catalyst precursor.

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The circulation flow was 30.0 l/h, corresponding to an LHSV of 3 h⁻¹. At a reactor pressure of 2 bar, a constant 30.0 standard l/h of nitrogen were metered in. After reaching 160°C, hydrogen addition was commenced. The initial amount of H₂ of 15 standard l/h was increased stepwise to 60 standard l/h. The water of reaction is partly carried out with the waste gas, another part remains in the catalyst bed.

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After 10 hours, the reduction of the catalyst precursor was complete (see Table 3).

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Table 3. Catalyst reduction in the liquid phase

Time in hours	Temperature	Hydrogen in standard l/h	Nitrogen in standard l/h
0-1.5 h	160	15	30
1.5-2.0 h	160	20	30
2.0-3.0 h	160	25	30
3.0-5.0 h	160	30	30
5.0-7.0 h	160	35	30
7.0-10 h	160	60	30

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The activity of the catalyst which had been reduced in this way was subsequently tested under the same conditions as those for the reduced catalyst from Example 1. The analyses of the starting material and product are shown in Table 4.

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Table 4. Activity determination for the catalyst reduced according to the invention

	1/LHSV $t_{cat} \cdot h /$ $t_{starting}$ material	Olefins % by weight	Pa- raffins % by weight	Alde- hydes % by weight	Alco-hols % by weight	High boilers % by weight
10 Starting material	0	14.8	1.2	76.5	4.5	3.0
Product	1.75	14.3	1.6	0.2	80.6	3.3

15 Tables 2 and 4 show that the activity of the catalyst which has been reduced according to the invention corresponds to that of a conventionally activated catalyst. At the same time, the reduction time was able to be reduced to about 18%.

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CLAIMS:

1. A process for reducing a nickel-containing catalyst, which comprises:
reducing a nickel-containing catalyst material in the liquid phase,
which comprises alcohols prepared by the hydrogenation of
aldehydes, of a single-stage process by means of hydrogen, thereby
producing a nickel-containing catalyst useful for the hydrogenation
of aldehydes, wherein the reactor containing the Ni-containing
catalyst is also employed for the hydrogenation of aldehydes to
alcohols product.
2. The process as claimed in Claim 1, wherein the reduction of the
nickel-containing catalyst is conducted at a temperature ranging
from 100 to 200° C and a pressure ranging from 1 to 25 bar.
3. The process as claimed in Claim 1, wherein the catalyst comprises
nickel, copper and chromium.