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Hydrogenation catalyst, a process for its preparation, and the use thereof

The present invention relates to a reduced hydrogenation catalyst comprising nickel, nickel oxide, magnesium oxide and a water-insoluble support material.

Catalysts based on nickel as active catalyst component for the hydrogenation of aldehydes are part of the prior art.

EP-A-0 322 049 describes a hydrogenation catalyst comprising

1) a molar ratio of SiO_2/Ni = 0.15 - 0.35
2) a molar ratio of (Mg; Ba)/Ni = 0 - 0.15,

in which part of the nickel is present in metallic form.

The known hydrogenation catalysts based on nickel can be used in the hydrogenation of aldehydes only at hydrogenation temperatures up to about 100°C, since increasing hydrogenation temperature leads to the formation of undesired by-products which can sometimes only be removed by a complicated distillation.

It was therefore an object of the invention to provide a hydrogenation catalyst which has high selectivity and conversions of over 99.5% at high throughput rates and hydrogenation temperatures above 110°C.

This object is surprisingly achieved by means of a hydrogenation catalyst containing

from 25 to 50% by weight of nickel (metallic)
from 10 to 35% by weight of nickel oxide
from 4 to 12% by weight of magnesium oxide

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from 1 to 5% by weight of sodium oxide
remainder support material,

where the total of nickel and nickel oxide is from 40 to 70% by weight, and having a surface area determined by BET from 80 to 200 m^2/g and a total pore volume determined by Hg porosimetry from 0.35 to 0.6 ml/g, with the total pore volume being made up of

from 30 to 60 percent by volume having a pore radius of ≤ 40 Å,
from 4 to 10 percent by volume having a pore radius of > 40 to 300 Å,
from 30 to 60 percent by volume having a pore radius of > 300 to 5000 Å.

The hydrogenation catalyst of the invention can alternatively and preferably have the following further characteristics:

a) from 5 to 10 atomic layers on the surface of the hydrogenation catalyst contain, determined by SAM analysis,
from 18 to 30, preferably from 20 to 28, atom% Ni
from 1.2 to 3.0, preferably from 1.5 to 2.5, atom% Na
from 2.8 to 4.8, preferably from 3.2 to 4.5, atom% Mg;

b) the metallic nickel surface area is, as determined by chemisorption of hydrogen, from 100 to 130 m^2/g Ni;

c) it contains aluminum oxide or silicon dioxide, particularly in the form of silicic acid, silica gel, kieselguhr or siliceous earth, as support material.

The invention further relates to a process for preparing

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the hydrogenation catalyst, which comprises preparing, in a precipitation step, a green catalyst from nickel salt, magnesium salt and sodium carbonate and also a support material, slurrying this green catalyst, after separating off the mother liquor and partial washing, in alkali solution, separating it from the liquid phase, drying and treating the dried green catalyst with hydrogen until from 42 to 83% by weight of the total nickel content is present in metallic form.

An alternative and preferred process method is one wherein

d) in the precipitation step, an aqueous solution containing from 0.5 to 0.8 mol/l of nickel salt and 0.1 to 0.2 mol/l of magnesium salt and at a temperature from 95 to 100°C is stirred into a from 0.9 to 1.1 molar sodium carbonate solution at a temperature from 95 to 100°C until the molar ratio of Na_2CO_3 : (Ni + Mg) = 1 : from 0.60 to 0.65 and subsequently the support material is immediately added over a period of from 0.5 to 5 minutes and the green catalyst formed is filtered off from the mother liquor and partially washed with hot water, until the wash water which runs off has a conductivity from 1500 to 2000 µS; the green catalyst is then suspended in from 1 to 3 times the amount of water and admixed by stirring with from 0.06 to 0.08 mol of sodium hydroxide solution or from 0.03 to 0.04 mol of sodium carbonate per mole of nickel used in the precipitation step, and after from 1 to 5 hours' stirring at a temperature from 40 to 60°C the green catalyst is separated off from the suspension;

e) the green catalyst which has been separated off from the suspension and dried is reduced at a temperature from 350 to 450°C by treating the dried green catalyst with from 0.5 to 5.0 standard m^3/h of reduction

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gas per kg of green catalyst, the reduction gas containing from 80 to 100% by volume of hydrogen;

f) from 1 to 3 standard m^3/h of reduction gas is used per kg of dried green catalyst.

For better shaping, from 0.5 to 5% by weight of graphite may be added to the hydrogenation catalyst.

The hydrogenation catalyst of the invention can be used for the hydrogenation of propanal and n-butanal and i-butanal, preferably at from 110 to 160°C.

With the hydrogenation catalyst of the invention, the hydrogenation of propanal and butanal can be carried out with simultaneous generation of steam under pressure to improve the economics of the hydrogenation. In comparison with conventional hydrogenation catalysts, the hydrogenation can be carried out at increased space velocities over the catalyst from 0.8 to 1.0 kg/h of aldehyde per kg of catalyst.

The selectivity is greater than 99.5%, mostly greater than 99.9%; about 0.01% of the aldehyde used remains in the final product. Less than 0.1% of the aldehyde is converted into carbon monoxide, ethers, acetals and esters.

In the hydrogenation of n-butanal, the formation of dibutyl ether is below 50 ppm, allowing distillation of the final product to be omitted.

In the hydrogenation of n-propanal, the formation of dipropyl ether is below 20 ppm.

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Analytical methods employed

1. BET determination of surface area

Method for determining the BET total surface area according to Brunauer, Emmett and Teller is described in J. Amer. Chem. Soc. 60 (1938), page 309.

2. Determination of pore volume by Hg porosimetry (total pore volume and pore distribution)

The method for the determination of pore volume by Hg porosimetry up to 3900 bar according to H.L. Ritter, L.C. Drake is described in Ind. Engng. chem. analyt. Edit, 17 (1945) 782.

3. Determination of surface area by chemisorption

The method for determining the surface area of the nickel by chemisorption, viz. the amount of hydrogen adsorbed at 20°C, is described in J. of Catalysis 81 (1983) 204 and 96 (1985) 517.

4. Determination of pore radius

The method for the determination of pore radius is described by S.J. Gregg, K.S.W. Sing, Adsorption Surface Area and Porosity, Academic Press New York-London (1967), pages 160 to 182.

5. Surface analysis by SAM spectroscopy (Scanning Auger Microprobe)

The analyses were carried out with a SAM spectrometer model PHI 660 from Perkin-Elmer.

The samples to be analyzed were evacuated down to a vacuum of $\leq 1 \times 10^{-8}$ torr in a sample chamber by means of a turbomolecular pump.

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An electron gun produced an electron beam which was fired at the sample. Because of strong charging of the samples by the stream of electrons, MULTIPLEX measurements were carried out at 5 different points on each sample, only the energy ranges of the elements to be expected being scanned, so as to achieve as short as possible a measurement time.

The SAM analysis method is described in "Practical surface analysis by Auger and X-ray photoelectronic spectroscopy" by D. Briggs and M. Seah, John Wiley and Sons, New York, London (1983), pages 217 ff. and 283 ff.

The measurement and analysis of the AUGER electrons emitted from the sample was carried out by means of a cylindrical mirror analyzer.

The following conditions were selected in the analyses:

Energy resolution (E/E):	0.6 %
Activation energy:	10 kV/10 mA
Lateral resolution:	about 220 nm

The quantitative evaluation was based on the sensitivity factors of the pure elements, which are published in "Handbook of Auger Spectroscopy".

The corresponding values for the elements nickel, sodium and magnesium were measured and evaluated.

Properties of the hydrogenation catalyst

The specific physical and chemical properties of the hydrogenation catalyst, which in the final analysis are the prerequisite for its advantageous hydrogenation behavior, are essentially achieved by the following features and measures in the preparation.

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In the precipitation step, the joint precipitation of mixed basic nickel-magnesium carbonate and the deposition thereof on the support material occur. The precipitation conditions are selected so that the proportion of the precipitate comprising basic magnesium carbonate is present in as sparingly soluble a form as possible.

The green catalyst obtained in the precipitation step is, according to the invention, only partially washed so that little precipitated basic magnesium carbonate is washed out of the green catalyst.

The invention includes the controlled subsequent alkalization of the partially washed green catalyst, whereby the required enrichment of the catalyst surface with alkali is achieved.

The drying of the green catalyst is not critical. It can be carried out within a relatively broad range of drying conditions, for example in a stream of air at from 50 to 100°C.

What is critical and inventive is the reduction of the green catalyst to the hydrogenation catalyst. The reduction is to be carried out in such a way that maintenance of the temperature at from 350 to 450°C and a hydrogen flow rate from 0.25 to 0.75 m/s results in only a partial reduction of the nickel-containing component. A degree of reduction from 42 to 83% has proven to be advantageous.

When used in fixed-bed hydrogenation, the green catalyst is shaped prior to drying, for example into extrudate, dried, reduced and used in this form or stabilized after reduction by treatment with small amounts of O_2 in N_2 in a known manner (H. Blume, W. Naundorf and A. Wrubel, Chem. Techn., volume 15 (1963), page 583).

It has been found that sodium depletion of the surface of the hydrogenation catalyst causes an increase in cleavage

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and secondary reactions which lead to loss of valuable products.

Excessive sodium concentrations at the surface of the hydrogenation catalyst results in an increasing decline in the hydrogenation activity. In addition, there is a tendency to form aldolization products.

Magnesium depletion of the surface of the hydrogenation catalyst leads to an altered pore structure which is unfavorable compared with the catalyst of the invention and to an increase in the catalyst activity which leads, in particular in the hydrogenation temperature range above 100°C, to the formation of undesired by-products, in particular of cleavage products; a large magnesium excess causes inactivation and thus lower performance of the hydrogenation catalyst.

The sodium content in the surface layer is required in the hydrogenation catalyst for controlling the selectivity and thus for suppressing cleavage and secondary reactions. The increased sodium concentration in the surface layer is achieved by slurrying the green catalyst in an alkali solution.

The examples below serve to clarify the present invention without limiting it.

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Example

Preparation of the hydrogenation catalyst

1906 g of $Ni(NO_3)_2 \cdot 6H_2O$ and 355.6 g of $Mg(NO_3)_2 \cdot 6H_2O$ are dissolved in 10.4 l of water at 99°C.
In a stirred reactor, 1500 g of anhydrous Na_2CO_3 are dissolved in 14 l of water at 99°C.

While stirring vigorously, the Ni-Mg solution is then allowed to run at a uniform rate into the sodium carbonate solution over 3 minutes. 230 g of kieselguhr are added in powder form and the suspension formed is first stirred for a further 3 minutes and subsequently filtered. The filter cake is washed with 27 l of water at a temperature of 70°C. The last wash water running off had a conductivity of 1800 µS.
The filter cake was suspended in 6000 g of 0.25% by weight strength sodium hydroxide solution and stirred for 2 hours at 50°C and filtered on a filter press. The filter cake is treated with compressed air for 1 minute. The moisture content of the filter cake was 82% water. In this form, the filter cake was formed into pellets (6 mm ø). The shaped filter cake was dried in a drying cabinet for 5 hours at 50°C, 3 hours at 60°C and for 8 hours at 75°C to constant weight.

The green catalyst had the following analysis:

Ni	37.8 % by weight
MgO	5.2 % by weight
Na_2O	1.1 % by weight
CO_2	6.0 % by weight
Support material	22.7 % by weight
Moisture	6.5 % by weight
Bulk density	530 g/l

The green catalyst was reduced at 425°C over a period of 4 hours. For this purpose, 6 standard m^3/h of reduction

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gas were passed over 2 kg of green pelletized catalyst. The reduction gas comprised 99.5% by volume of hydrogen and 0.5% by volume of nitrogen.

A weight loss of 0.76 kg was observed on reduction.

For a total nickel content of 53% by weight, a degree of reduction of 72% was determined in the reduced catalyst.

Application Example 1
Hydrogenation of n-butanal

The catalyst prepared according to Example 1, in the form of 6 mm pellets (250 ml), is first brought to 120°C at a heating rate of 20°C/h in a stream of hydrogen of 730 standard l/h at 4 bar in a tube reactor provided with a heating/cooling jacket (internal diameter: 32 mm). After reaching 120°C, 50 ml/h of n-butanal (liquid) are fed into the vaporizer which is upstream of the reactor and through which 730 standard l/h of H_2 flow, at a vaporizer temperature of 100°C. The H_2/butanal-vapor mixture is heated to reactor temperature in a preheater upstream of the reactor. After 12 hours, the n-butanal feed rate is increased to 75 ml/h and after a further 12 hours increased to 100 ml/h. Thereafter, the butanal feed is increased in steps of 25 ml of n-butanal at intervals of 24 hours. During the increase in the butanal feed, the preheater and reactor temperatures are simultaneously increased as follows:

n-Butanal feed (ml/h)	Time (h)	Preheater/reactor temperature (°C)
200	24	123
225	24	126
250	continuous operation	128

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The amount of H_2 is kept constant during the running-up period and during continuous operation.
The hydrogenation product obtained in vapor form is condensed and analyzed.
The hydrogenation product comprises 99.9% by weight of n-butanol and contains less than 0.1% by weight of unconverted n-butanal as well as < 20 ppm of di-n-butyl ether as by-product.
In addition to the hydrogenation product, about 0.4 kg of steam per kg of n-butanal used is obtained at > 1.8 bar during continuous operation (steam pressure corresponding to the reactor temperature).

Application Example 2
Hydrogenation of propanal

The catalyst prepared according to Example 1, in the form of 6 mm pellets (250 ml), is first heated to 125°C at a heating rate of 20°C/h in a stream of hydrogen (730 standard l/h) at 3.5 bar in the same reactor system as in Application Example 1. Propanal (liquid) is then fed into the vaporizer at an initial rate of 50 ml/h for a period of 12 hours. The propanal feed rate is increased at intervals of 12 hours by 25 ml/h each time up to a rate of 150 ml/h. On reaching the feed rate of 150 ml/h, the preheater and reactor temperatures are increased to from 128 to 130°C. The hydrogenation product obtained is condensed by cooling and analyzed. It comprises about 99.9% by weight of n-propanol and < 0.1% by weight of unconverted propanal. By-products determined are < 100 ppm of 2-methylpentan-3-one and < 20 ppm of di-n-propyl ether.
As in Application Example 1, it is also possible to obtain steam (≥ 1.3 bar) in the hydrogenation of propanal with the catalyst of the invention.

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Application Example 3
Hydrogenation of i-butanal

For the hydrogenation of i-butanal, the catalyst (250 ml) from Example 1 was heated to 120°C under H_2 under the same conditions as in Application Example 1. Subsequently, 50 ml/h of i-butanal were fed in. Hydrogenation pressure (3.5 bar), reactor temperature (120°C) and H_2 feed rate (730 standard l/h) were kept constant.
The hydrogenation product obtained comprised ≥ 99.95% by weight of i-butanol and contained ≤ 0.03% by weight of unconverted i-butanal and < 20 ppm of di-i-butyl ether. The hydrogenation of i-butanal on the catalyst of the invention gave steam at ≥ 1.8 bar.

Comparative Example
Hydrogenation of n-butanal

In the same tube reactor as in Application Example 1, 250 ml of the commercial nickel catalyst 55/5 TST (HOECHST AG) in the form of 6 mm pellets are heated to 100°C at a heating rate of 20°C/h in a stream of hydrogen of 730 standard l/h at 3.5 bar.
50 ml/h of n-butanal (liquid) were then fed into the vaporizer upstream of the reactor, the vaporizer being at 100°C and having 730 standard l/h of H_2 flowing through it. Prior to entering the reactor, the H_2/butanal-vapor mixture is heated to reactor temperature in a preheater. After 12 hours the feed rate of n-butanal is increased to 75 ml/h, and is increased at intervals of 12 hours up to a rate of 150 ml/h. These reaction conditions resulted in a hydrogenation product which comprised 98.9% by weight of n-butanol, 0.3% by weight of acetals, 0.3% by weight of trimeric aldolization products of the butanal, 0.1% by weight of hydrocarbons, 0.1% by weight of 2-ethylhexanol, 0.1% by weight of di-n-butyl ether and from 200 to 300 ppm of C_4/C_4 esters.
Of the n-butanal used, from 1.0 to 1.2% by weight were converted via hydrogenolysis into propane and methane

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which are contained in the outflowing hydrogenation hydrogen.

In contrast to the catalyst of the invention, use of the commercial catalyst gave considerable proportions of by-products even at 100°C. A particular difficulty in the isolation of pure n-butanol is the distillative removal of the di-n-butyl ether, which with increasing ester contents leads to disproportionate losses of n-butanol.

A further disadvantage, compared with the catalyst of the invention, is the relatively high loss of desired product (> 1% by weight) caused by hydrogenolysis.

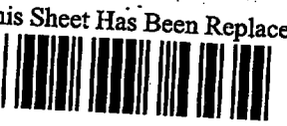
If the feed of n-butanal is increased to above 150 ml/h, there is a rise particularly in the formation of di-n-butyl ether and cleavage products as a result of hydrogenolysis.

The same effects occur on raising the hydrogenation temperature.

In comparison with the catalyst of the invention, the catalyst of the prior art enables a maximum conversion of only 60% of the amount of aldehyde, with the hydrogenation products obtained also being more contaminated.

A further disadvantage is the limiting of hydrogenation temperature to a maximum of 100°C, at which no usable steam can be obtained.

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Hydrogenation catalyst, a process for its preparation, and the use thereof

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WHAT IS CLAIMED IS:

1. A hydrogenation catalyst comprising nickel, nickel oxide, magnesium oxide, sodium oxide and a water-insoluble support material, said hydrogenation catalyst containing

from 25 to 50 % by weight of nickel (metallic)
from 10 to 35 % by weight of nickel oxide
from 4 to 12 % by weight of magnesium oxide
from 1 to 5 % by weight of sodium oxide
remainder support material,

where the total of nickel and nickel oxide is from 40 to 70% by weight, and having a surface area determined by BET from 80 to 200 m^2/g and a total pore volume determined by Hg porosimetry from 0.35 to 0.6 ml/g, with the total pore volume being made up of

from 30 to 60 percent by volume having a pore radius of ≤ 40 Å,
from 4 to 10 percent by volume having a pore radius of > 40 to 300 Å,
from 30 to 60 percent by volume having a pore radius of > 300 to 5000 Å.

2. A hydrogenation catalyst as claimed in claim 1, wherein 5-10 atomic layers on the surface of the hydrogenation catalyst contain, determined by SAM analysis,
from 18 to 30, preferably from 20 to 28, atom% Ni
from 1.2 to 3.0, preferably from 1.5 to 2.5, atom% Na
from 2.8 to 4.8, preferably from 3.2 to

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4.5, atom% Mg.

3. A hydrogenation catalyst as claimed in either of claims 1 and 2, wherein the metallic nickel surface area is, as determined by chemisorption of hydrogen, from 100 to 130 m^2/g Ni.

4. A hydrogenation catalyst as claimed in any of claims 1 to 3, which contains aluminum oxide or silicon dioxide, particularly in the form of silicic acid, silica gel, kieselguhr or siliceous earth, as support material.

5. A process for preparing the hydrogenation catalyst as claimed in at least one of claims 1 to 4, which comprises preparing, in a precipitation step, a green catalyst from nickel salt, magnesium salt and sodium carbonate and also a support material, slurrying this green catalyst, after separating off the mother liquor and partial washing, in alkali solution, separating it from the liquid phase, drying and treating the dried green catalyst with hydrogen until from 42 to 83% by weight of the total nickel content is present in metallic form.

6. The process as claimed in claim 5, wherein, in the precipitation step, an aqueous solution containing from 0.5 to 0.8 mol/l of nickel salt and 0.1 to 0.2 mol/l of magnesium salt and at a temperature from 95 to 100°C is stirred into a from 0.9 to 1.1 molar sodium carbonate solution at a temperature from 95 to 100°C until the molar ratio of Na_2CO_3 : (Ni + Mg) = 1 : from 0.60 to 0.65 and subsequently the support material is immediately added over a period of from 0.5 to 5 minutes and the green catalyst formed is filtered off from the mother liquor and partially washed with hot water, until the wash water which runs off has a conductivity from 1500 to 2000 μS; the green catalyst is

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then suspended in from 1 to 3 times the amount of water and admixed by stirring with from 0.06 to 0.08 mol of sodium hydroxide solution or from 0.03 to 0.04 mol of sodium carbonate per mole of nickel used in the precipitation step, and after from 1 to 5 hours' stirring at a temperature from 40 to 60°C the green catalyst is separated off from the suspension.

7. The process as claimed in either of claims 5 and 6, wherein the green catalyst which has been separated off from the suspension and dried is reduced at a temperature from 350 to 450°C by treating the dried green catalyst with from 0.5 to 5.0 standard m^3/h of reduction gas per kg of green catalyst, the reduction gas containing from 80 to 100% by volume of hydrogen.

8. The process as claimed in claim 7, wherein from 1 to 3 standard m^3/h of reduction gas are used per kg of dried green catalyst.

9. A method of using the hydrogenation catalyst for the hydrogenation of propanal, n-butanal and i-butanal.

10. A method of using the hydrogenation catalyst as claimed in claim 9, wherein the hydrogenation catalyst is used at from 100 to 160°C.

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