

REPLACED SHEETS		SG
✓ Description : page 1 to page 19		
✓ Claim(s) : page 42 to page 42		
✓ Drawing(s) : page 4 to page 4		
✓ Abstract : page 4 to page 4		
DATE OF RECEIPT		

Process for the preparation of alcohols or amines

The present invention relates to a process for the preparation of alcohols or amines by reaction of esters, fatty acids or nitriles with hydrogen at elevated temperature and under pressure in the presence of a copper-containing catalyst. The catalyst is notable for a comparatively high BET total area and a particular pore-radius distribution, expressed in terms of the proportion of the BET total area resulting from pores of a particular size. The catalyst is prepared by precipitating from an aqueous solution, which contains a copper salt and salts of further elements, a coprecipitate by means of a basic precipitant, and by then washing, drying and calcining the coprecipitate. The catalyst does not contain chemically bound chromium.

Copper-containing catalysts are used in industrial processes to a considerable extent. For example, they play an important part in hydrogenation and dehydrogenation processes. In this instance, the feedstock to be reacted is passed to the fixed catalyst either in the gaseous state (gas-phase operational mode) or in the liquid state (liquid-phase operational mode). The catalyst can also be used in a finely disperse state as a suspension (suspension operational mode).

Very wide use has been made of catalysts which, in addition to copper, also contain chromium, inter alia for the hydrogenation of esters. These catalysts are also known under the designation copper chromite catalysts or Adkins catalysts.

However, the use of Adkins catalysts is not without problems, because their preparation makes use of chromium(VI) compounds which have to be considered as carcinogenic and which, in handling them, require appropriate protective measures. Furthermore, in the course of



WERK RUHRCHEMIE FFR

- 2 -

the preparation relatively large quantities of waste waters are produced which are heavily polluted with compounds of copper, chromium(VI) and ammonium. Waste waters of this type are undesirable, because compounds of both copper and chromium(VI) are highly toxic to micro-organisms and must be removed from the waste water by laborious treatment.

Occasional use is also made of copper catalysts containing no chemically bound chromium for the hydrogenation of esters. According to US-A 4,199,479, supported catalysts containing copper, zinc oxide and, if required, cobalt are suitable for this purpose. EP-B 0,074,193 describes a process for the hydrogenation of esters in the gas phase by means of a catalyst containing copper and zinc oxide.

Chromium-free copper catalysts are also often recommended for other reactions.

Thus DE-OS 2,056,612 describes a catalyst comprising mixed crystals from the series $(\text{Cu}_x\text{Zn}_y)\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, where x and y can assume numerical values from 0.5 to 5.5 and the sum x plus y equals 6. The mixed crystals are obtained by a precipitation at a pH between 4.5 and 5.5, by adding to an aqueous solution containing nitrates of copper, zinc and aluminum a basic precipitant, for example an aqueous Na_2CO_3 solution.

The catalyst, which in the non-reduced form contains CuO , ZnO and Al_2O_3 , is used in the conversion of a gas mixture comprising carbon monoxide, carbon dioxide and hydrogen, to give methanol.

EP. 0,125,689 relates to a catalyst containing CuO , ZnO and Al_2O_3 , having an atomic ratio $\text{Cu}:\text{Zn}$ 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 from



WERK RUHRCHEMIE FFR

- 3 -

8 to 12% by weight. Al_2O_3 is used in the preparation as colloidal aluminum hydroxide, Cu and Zn are incorporated in the catalyst by precipitation from metal salt solutions. The catalyst is used for the production of methanol.

It is an object of the present invention to provide a process which makes it possible not only to produce alcohols by catalytic hydrogenation of esters and fatty acids, but also to produce amines by catalytic hydrogenation of nitriles, by means of a chromium-free copper catalyst. Furthermore, the process should ensure that the reaction, in particular at elevated temperatures, proceeds with high yield and high selectivity and very largely avoids the formation of by-products, the results achievable with conventional Adkins catalysts not only being equalled, but in many cases even being distinctly improved upon. A further advantage is found in the fact that the preparation of the chromium-free copper catalyst circumvents problems which are significant in the preparation of Adkins catalysts, such as the handling of carcinogenic chromium(VI) compounds, the production of waste waters containing noxious compounds, and the safe disposal of chromium-containing used catalysts.

The objects are achieved by a process for the preparation of alcohols or amines by reaction of esters, fatty acids or nitriles with hydrogen under pressure and elevated temperature in the presence of a copper-containing catalyst, wherein the catalyst in the non-reduced state, per 100 parts by weight of CuO , comprises 40 to 130 parts by weight of ZnO , 2 to 50 parts by weight of Al_2O_3 and optionally 0.5 to 8 parts by weight of oxide of Mn, Mo, V, Zr and/or alkaline earth metal, has a BET total area of 80 to 175 m^2 per gram of catalyst in the non-reduced state, 75 to 95% of the BET total area being formed by pores having a radius $r_p \leq 15$ nm.



- 4 -

A further feature of the process according to the invention is a relatively large active copper metal surface area of the catalyst. In the reduced catalyst said area is 30 to 125, in particular 35 to 100, preferably 40 to 85 m² per gram of Cu and thereby exceeds the active copper metal surface area of corresponding copper chromite catalysts. The determination method can be found in 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, from 40 to 130, in particular from 45 to 100, preferably from 45 to 80 parts by weight of ZnO, and from 2 to 50, in particular from 3 to 40, preferably from 4 to 30, particularly preferably from 4 to 11 parts by weight of Al₂O₃.

If required, the catalyst comprises further substances. These include oxides of manganese, molybdenum, vanadium, zirconium and/or of an alkaline earth metal. Per 100 parts by weight of CuO, their proportion is from 0.5 to 8, particularly from 1 to 6, preferably from 2 to 4 parts by weight, calculated as MnO, MoO₃, V₂O₅, ZrO₂ and MeO, where Me is an alkaline earth metal.

Particularly suitable further substances are manganese oxide and/or an alkaline earth metal oxide. Possible alkaline earth metal oxides are oxides of Mg, Ca or Ba, in particular Ca oxide or Ba oxide, preferably Ba oxide.

A further feature of the process according to the invention is the comparatively high BET total area of the catalyst. Said area is from 80 to 175, in particular from 85 to 160, preferably from 90 to 155 m² per gram of catalyst in the non-reduced state.



WERK RUHRCHEMIE FFR

- 5 -

The BET total area is to be understood as the area measured by adsorption of nitrogen according to the method of Brunauer, Emmett and Teller (BET). The method for determining the BET total area is described in J. Amer. Chem. Soc., 60, (1938) 309.

An additional feature of the catalyst used according to the invention is a particular pore-radius distribution, expressed in terms of a high proportion of the BET total area which is formed by pores having a radius $r_p \leq 15$ nm (150 Å). Their proportion is from 75 to 95, in particular from 80 to 92, preferably from 84 to 90% of the BET total area.

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

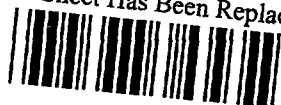
The range of the pores whose radius r_p is between 9 and 15 nm is covered by from 5 to 45, in particular from 15 to 40, preferably from 18 to 30% of the BET total area.

It should again be noted here that the abovementioned data regarding the BET total area in each case relate to the catalyst in the non-reduced form.

The pore radii are determined by evaluation of the desorption isotherms with the aid of the Kelvin equation according to C. Pierce, J. Phys. Chem. 57, (1953) 149. The data regarding the pore radii also relate to the non-reduced catalyst.

If required, the catalyst may also, in addition to the components already mentioned, comprise a support. Per 100 parts by weight of CuO, it comprises from 2 to 80, in particular from 4 to 60, preferably from 5 to 35 parts by weight of support. The support may comprise conventional water-insoluble materials. Suitable support materials are

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WERK RUHRCHEMIE FFR

- 6 -

SiO₂, kieselguhr, silica gel and Al₂O₃, in particular Al₂O₃.

The catalyst in reduced form, per 100 parts by weight of Cu, comprises from 48 to 163, in particular from 56 to 125, preferably from 56 to 100 parts by weight of ZnO, from 2.4 to 63, in particular from 3.7 to 50, preferably from 5.0 to 37.5, particularly preferably from 5 to 13.8 parts by weight of Al₂O₃, and where appropriate, from 0.6 to 10, in particular from 1.2 to 7.5, preferably from 2.4 to 5.0 parts by weight of oxides of Mn, Mo, V, Zr and/or alkaline earth metal.

Below, the preparation of the chromium-free copper catalyst will also be described in more detail. The starting material is an aqueous solution containing salts of copper, zinc, aluminum and, if appropriate, of Mn, Mo, V, Zr and/or alkaline earth metals. This solution, also designated below as mixed salt solution, contains from 10 to 100 g of Cu/l, from 10 to 50 g of Zn/l, and Al corresponding to from 2 to 80 g of Al₂O₃/l. If required, the mixed salt solution additionally contains from 3 to 80 g of Mn, Mo, V, Zr and/or alkaline earth metal per liter, calculated as MnO, MoO₃, V₂O₅, ZrO₂ and MeO, where Me is an alkaline earth metal.

The mixed salt solution is prepared by dissolving water-soluble salts of the abovementioned elements in water. Nitrates have proved to be particularly useful.

It is advisable to set the pH of the mixed salt solution to below 4.0, adding acid if required.

The precipitant used is an aqueous solution of a basic compound, usually an aqueous alkali metal carbonate or alkali metal hydrogen carbonate solution.



WERK RUHRCHEMIE FPR

- 7 -

In order to ensure as complete a precipitation as possible, and to obtain, at the same time, a particularly homogeneous coprecipitate, the basic compound is used in stoichiometric excess.

- 5 The precipitation is achieved in that the mixed salt solution and the precipitant, separate from one another but simultaneously, are brought together, continuously or batchwise, under conditions of vigorous mixing.

10 The coprecipitate is precipitated by bringing the mixed salt solution and the precipitant together comparatively slowly. The precipitation time should be at least 10 minutes.

15 During the precipitation, a constant pH within a pH range from 6.5 to 8.5, in particular from 7.6 to 8.0, is applied. Fluctuations of the pH should be kept as low as possible.

The precipitation is carried out at constant temperatures above 70°C, in particular in a range from 75 to 95°C.

20 After the precipitation, the coprecipitate is separated from the mother liquor and is carefully washed.

In general it is sufficient to maintain, during the washing process, a temperature from 55 to 85, in particular from 60 to 75°C, and to use from 5 to 50 kg of wash water per kg of coprecipitate.

25 The duration of the washing process must be sufficiently long. It should be at least 60 minutes.

30 It has proved to be sufficient to dry the coprecipitate at temperatures from 50 to 120°C, until a residual moisture content of approximately 2 to 15% by weight of water, based on the dried coprecipitate, is achieved.



WERK RUHRCHEMIE FPR

- 8 -

The subsequent calcination takes place at from 250 to 450°C, over a period from 3 to 10 hours. The calcined catalyst can either be used in powdered form, directly for suspension hydrogenations, or after shaping, such as
5 tableting or pelleting, as a fixed catalyst.

The process according to the invention is suitable, on the one hand, for the production of alcohols by hydrogenation of the corresponding esters or fatty acids, and, on the other hand, for the production of amines by
10 hydrogenation of nitriles. The feedstock materials need not meet any particular requirements, for example with regard to composition or purity. They can be used in the form of the generally available technical grades. Even
15 feedstock materials which, because of particular impurities such as, for example, sulfur-containing compounds, are regarded as being difficult to hydrogenate, can be used successfully in the process according to the invention.

The process according to the invention requires somewhat
20 different reaction conditions for the production of alcohols, compared to the production of nitriles. If alcohols are to be produced, the corresponding esters or fatty acids are reacted at from 200 to 350, in particular at from 220 to 330, preferably at from 230 to 320°C. The
25 pressure is usually from 15 to 40, in particular from 18 to 35, preferably from 20 to 32 MPa.

The feedstock materials used are esters of carboxylic acids having from 2 to 30 carbon atoms, in particular of naturally occurring carboxylic acids, having from 8 to
30 30, in particular from 10 to 24, preferably from 12 to 22 carbon atoms. These include esters which are formed from the abovementioned carboxylic acids and monohydric alcohols having 1 to 4 carbon atoms on the one hand, and polyhydric alcohols having 2 to 6 carbon atoms on the
35 other hand.



- 9 -

Of industrial significance are the methyl and butyl esters of the abovementioned carboxylic acids.

5 Examples of suitable esters are methyl oleate, ester mixtures of tallow fat acid, palm oil acid, palm kernel oil acid, and coconut oil acid, in particular the methyl esters thereof.

10 Another possible feedstock material comprises fatty acids. The fatty acids contain from 8 to 30, in particular from 10 to 24, preferably from 12 to 22 carbon atoms. They can be saturated, singly unsaturated or multiply unsaturated.

Examples of suitable fatty acids are oleic acid, tallow fat acid, palm oil acid, palm kernel oil acid and coconut oil acid.

15 For the production of amines, nitriles are usually reacted under somewhat milder conditions than the esters and fatty acids. Temperatures of from 160 to 250, in particular of from 190 to 240, preferably of from 210 to 230°C, and pressures of from 0.5 to 10, in particular of
20 from 1.0 to 5.0, preferably of from 1.2 to 3.0 MPa, constitute suitable reaction conditions. Nitriles having from 4 to 30, in particular from 8 to 24, preferably from 10 to 22 carbon atoms can be converted in this manner into the corresponding amines.

25 Examples of suitable nitriles are propionitrile, butyronitrile, valeronitrile, capronitrile, caprylonitrile, laurionitrile, myristonitrile, palmitonitrile, oleonitrile, stearonitrile, alkylaminonitriles having 2 to 6 carbon atoms in the alkyl chain, and aliphatic, cyclo-
30 aliphatic and aromatic dinitriles, such as adiponitrile and isophorone dinitrile.



- 10 -

Experimental sectionExample 1Hydrogenation of a fatty-acid methyl ester mixture containing predominantly methyl oleate

5 The feedstock used is a fatty-acid methyl ester mixture consisting predominantly of methyl oleate (designation Estol 1400, commercially available from Unilever) which has the following composition (determined by gas-chromatographic analysis):

10	C ₁₂ -acid methyl ester	0.5% by weight
	C ₁₄ -acid methyl ester	4.5% by weight
	C ₁₆ -acid methyl ester	11.5% by weight
	C ₁₈ -acid methyl ester	approx. 81.0% by weight
	C ₂₀ -acid methyl ester	approx. 0.8% by weight
15	(remaining components not identified)	

The fatty-acid methyl ester mixture, because of its sulfur content (25 ppm by weight of S) is difficult to hydrogenate.

20 The catalyst I required for the reaction is prepared as follows:

By dissolving appropriate amounts of Cu(NO₃)₂ · 3H₂O, Zn(NO₃)₂ · 6H₂O and Al(NO₃)₃ · 9H₂O in water, a solution (mixed salt solution) is prepared. The basic precipitant used is an aqueous Na₂CO₃ solution. The mixed salt solution heated to 80°C, and the basic precipitant similarly heated to 80°C, in separate streams are brought together simultaneously with stirring, the mixture is filtered and the precipitate (coprecipitate) is washed with hot water. The washed filter cake is dried to a final moisture content of ≤ 5% by weight, based on the catalyst mass, and is subsequently calcined in an N₂ stream at 380°C.

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WERK RUHRCHEMIE FFR

- 11 -

The calcined catalyst I used for the reaction contains, in the non-reduced state, 59.2% by weight of CuO (corresponding to 47.3% by weight of Cu) and, per 100 parts by weight of CuO, contains 52.4 parts by weight of ZnO and 8.4 parts by weight of Al₂O₃.

The BET total area is 126 m² per gram of catalyst in the non-reduced state. 89% of the BET total area are formed by pores having a radius $r_p \leq 15$ nm, and 76% of the BET total area are formed by pores having a radius $r_p \leq 9$ nm. The copper metal area of the reduced catalyst is 78 m² per gram of Cu.

An autoclave (volume 1 liter) equipped with an oscillating magnetic stirrer is charged, while air is excluded, with 400 g of the previously described fatty-acid methyl ester mixture and 4 g of catalyst I. The vessel is then pressurized with hydrogen to a pressure of 18 MPa and heated while stirring (100 strokes per minute) to 250°C in 50 minutes. During heating, the pressure rises to 25 MPa. By pressurizing repeatedly with hydrogen, the pressure is kept constant at 25 MPa. After a reaction time of 125 minutes, hydrogen is no longer taken up. The reaction is complete. The autoclave is depressurized and cooled down.

Comparative Examples 1 to 5

25 Hydrogenation of a fatty-acid methyl ester mixture containing predominantly methyl oleate

The same procedure is followed as in Example 1, but in each case, 4 g of a commercially available catalyst are used. The reaction is halted after 125 minutes. At that time, the hydrogen uptake has not yet finished.

The following catalysts are used:

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- 12 -

Catalyst A in Comparative Example 1:

A copper chromite catalyst containing 42% by weight of Cu and 26% by weight of Cr.

Catalyst B in Comparative Example 2:

- 5 A copper chromite catalyst containing 36% by weight of Cu, 32% by weight of Cr, 2.2% by weight of Ba and 2.4% by weight of Mn. The BET total area is 30 m² per gram of catalyst.

Catalyst C in Comparative Example 3:

- 10 A copper chromite catalyst containing 36% by weight of Cu, 32% by weight of Cr, 2.2% by weight of Ba and 2.4% by weight of Mn. The BET total area is 65 m² per gram of catalyst.

Catalyst D in Comparative Example 4:

- 15 A copper chromite catalyst containing 36% by weight of Cu, 33% by weight of Cr and 3% by weight of Mn.

Catalyst E in Comparative Example 5:

- 20 A copper chromite catalyst containing approximately 47% by weight of CuO, approximately 49% by weight of Cr₂O₃ and approximately 4% by weight of MnO₂. The BET total area is 30 m² per gram of catalyst.

Example 2**Hydrogenation of a fatty-acid methyl ester mixture containing predominantly methyl oleate**

- 25 The same procedure is followed as in Example 1, except that the reaction is carried out at 300°C and 27 MPa. Hydrogenation is complete after as little as 45 minutes.



- 13 -

Comparative Example 6Hydrogenation of a fatty-acid methyl ester mixture
containing predominantly methyl oleate

5 The same procedure is followed as in Example 2, except
that 4 g of catalyst B are used. However, hydrogen uptake
is only complete after 90 minutes.

The results of Examples 1 and 2 and of Comparative
Examples 1 to 6 are summarized in the following Table 1.

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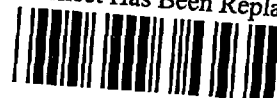


Table 1

	Example	Comparative Examples					Example	Comparative Example
	1	1	2	3	4	5	2	6
Catalyst	I	A	B	C	D	E	I	B
Temperature (°C)	250	250	250	250	250	250	300	300
Pressure (MPa)	25	25	25	25	25	25	27	27
Reaction time (min)	125	125	125	125	125	125	45	90
Composition of the reaction product (in % by weight)								
C ₁₂ - alcohol	0.5	0.3	0.4	0.4	0.3	0.3	0.5	0.5
C ₁₄ - alcohol	4.3	2.9	1.4	1.3	1.8	1.0	4.5	3.5
C ₁₆ - acid methyl ester	0.2	10.5	9.1	9.3	7.1	8.7	0.1	1.3
C ₁₆ - alcohol	11.2	0.7	2.0	2.6	3.9	1.9	10.8	10.1
C ₁₈ - acid methyl ester	1.3	74.9	66.0	59.6	57.2	67.6	1.0	2.8
C ₁₈ - alcohol	78.2	3.7	13.0	6.5	22.6	11.4	78.7	75.5
C ₂₀ - alcohol	0.6	0.2	0.3	0.2	0.1	0.3	0.5	0.3

- 15 -

Example 3Hydrogenation of a fatty-acid methyl ester mixture containing predominantly methyl laurate and methyl myristate

- 5 The feedstock used is a fatty-acid methyl ester mixture (coconut methyl ester) consisting predominantly of methyl laurate (C_{12} -acid methyl ester) and of methyl myristate (C_{14} -acid methyl ester) which has the following composition (determined by gas-chromatographic analysis):

10	C_{10}/C_{11} -acid methyl ester	0.7% by weight
	C_{12} -acid methyl ester approx.	55.0% by weight
	C_{14} -acid methyl ester approx.	21.0% by weight
	C_{16} -acid methyl ester approx.	10.0% by weight
	C_{18} -acid methyl ester approx.	13.0% by weight

- 15 The catalyst II required for the reaction is prepared in analogy to the preparation of the catalyst I described in Example 1.

- 20 The calcined catalyst II, in the non-reduced state, contains 58.6% by weight of CuO (corresponding to 46.9% by weight of Cu) and, per 100 parts by weight of CuO , contains 50.2% parts by weight of ZnO , 8.0 parts by weight of Al_2O_3 , and 2.6 parts by weight of BaO .

- 25 The BET total area is 118 m^2 per gram of catalyst in the non-reduced state. 87% of the BET total area are formed by pores having a radius $r_p \leq 15 \text{ nm}$, and 74% of the BET total area are formed by pores having a radius $r_p \leq 9 \text{ nm}$. The copper metal surface area of the reduced catalyst is 74 m^2 per gram of Cu .

- 30 An autoclave (volume 1 liter) equipped with an oscillating magnetic stirrer is charged, while air is excluded, with 400 g of the previously described fatty-acid methyl

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- 16 -

ester mixture (coconut methyl ester) and 4 g of catalyst II. The vessel is then pressurized with hydrogen to a pressure of 18 MPa and heated while stirring (100 strokes per minute) to 250°C in 50 minutes. During heating, the pressure rises to 25 MPa. By pressurizing repeatedly with hydrogen, the pressure is kept constant at 25 MPa. After a reaction time of 75 minutes, hydrogen is no longer taken up. The reaction is complete. The autoclave is depressurized and cooled down.

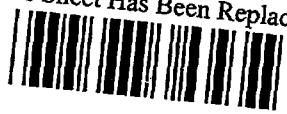
10 Comparative Examples 7 and 8

Hydrogenation of a fatty-acid methyl ester mixture containing predominantly methyl laurate and methyl myristate

15 The same procedure is followed as in Example 3, except that 4 g of catalyst B (Comparative Example 7) and 4 g of catalyst D (Comparative Example 8) are used. However, in both the Comparative Experiments 7 and 8, only after a reaction time of 135 minutes is there no further hydrogen uptake.

20 The results of Example 3 and of Comparative Examples 7 and 8 are summarized in the following Table 2.

This Sheet Has Been Replaced



- 17 -

Table 2

		Example	Comparative Example	
		3	7	8
5	Catalyst	II	B	D
	Temperature (°C)	250	250	250
	Pressure (MPa)	25	25	25
	Reaction time (min)	75	135	135
10	Composition of the reaction product (in % by weight)			
	C ₁₀₋₁₁ -alcohol	0.7	0.4	0.5
15	C ₁₂ -acid methyl ester	1.0	35.3	28.6
	C ₁₂ -alcohol	~54	20.7	25.5
	C ₁₄ -acid methyl ester	0.5	14.5	12.4
	C ₁₄ -alcohol	20.5	6.5	8.5
	C ₁₆ -acid methyl ester	0.3	7.2	6.8
20	C ₁₆ -alcohol	~10	2.8	3.7
	C ₁₈ -acid methyl ester	0.4	9.4	9.7
	C ₁₈ -alcohol	12.5	2.9	4.1

Example 425 Hydrogenation of palm kernel oil acid

The feedstock used is non-esterified palm kernel oil acid having the following characteristics:

Iodine number: 13.0 g I₂/100 g

Acid number: 267 mg KOH/g

30 An autoclave (volume 1 liter) equipped with an oscillating magnetic stirrer is charged, while air is excluded, with 400 g of the previously described palm kernel oil



- 18 -

acid and 32 g of catalyst I. The vessel is then pressurized with hydrogen to a pressure of 18 MPa and heated while stirring (100 strokes per minute) to 300°C in 90 minutes. During heating, the pressure rises to 27 MPa.

- 5 By pressurizing repeatedly with hydrogen, the pressure is kept constant at 27 MPa. After a reaction time of 100 minutes, hydrogen is no longer taken up. The reaction is complete. The autoclave is depressurized and cooled down.

Comparative Example 9

10 Hydrogenation of palm kernel oil acid

The same procedure is followed as in Example 4, except that 32 g of a commercially available copper chromite catalyst are used which contains 35.5% by weight of Cu, 32.6% by weight of Cr and 4.2% by weight of Ba (catalyst F).

The results of Example 4 and Comparative Example 9 are summarized in the following Table 3.

Table 3

	Example 4	Comparative Example 9
Catalyst	I	F
Temperature (°C)	300	300
Pressure (MPa)	27	27
Reaction time (min)	100	100
Characteristics of the reaction product		
Iodine number (g I ₂ /100 g)	0.12	1.9
Acid number (mg KOH/g)	0.39	5.8
Hydroxyl number (mg KOH/g)	273	209



- 19 -

Example 5Hydrogenation of a fatty acid nitrile

5 The feedstock used is tallow fat acid nitrile having an iodine number of 55.3 g I₂/100 g.

10 An autoclave (volume 1 liter) equipped with an oscillating magnetic stirrer is charged, while excluding air, with 400 g of tallow fat acid nitrile and 10 g of catalyst I. The reaction is carried out at 220°C and 1.5 MPa. After a reaction time of 240 minutes, hydrogen is no longer taken up. The reaction is complete. The autoclave is depressurized and cooled down.

15 The reaction product contains 63.8% by weight of primary fatty amine, 34.5% by weight of secondary fatty amine and 1.5% by weight of tertiary fatty amine. The residual iodine number is 52.6 g I₂/100 g.



Claims

1. A process for the preparation of alcohols or amines by reaction of esters, fatty acids or nitriles with hydrogen under pressure and elevated temperature in the presence of a copper-containing catalyst, wherein the catalyst in the non-reduced state, per 100 parts by weight of CuO, comprises 40 to 130 parts by weight of ZnO, 2 to 50 parts by weight of Al₂O₃ and optionally 0.5 to 8 parts by weight of oxide of Mn, Mo, V, Zr and/or alkaline earth metal, has a BET total area of 80 to 175 m² per gram of catalyst in the non-reduced state, 75 to 95% of the BET total area being formed by pores having a radius $r_p \leq 15$ nm.
2. The process 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 m² per gram of Cu.
3. The process as claimed in claim 1 or 2, wherein the catalyst in the non-reduced state, per 100 parts by weight of CuO, comprises 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 Al₂O₃.
4. The process as claimed in one or more of claims 1 to 3, wherein the catalyst has a BET total area of 85 to 160, in particular 90 to 155 m² per gram of catalyst in the non-reduced state.
5. The process as claimed in one or more of claims 1 to 4, wherein 80 to 92, in particular 84 to 90% of the BET total area are formed by pores having a radius $r_p \leq 15$ nm.
6. The process as claimed in one or more of claims 1 to 5, wherein the catalyst, per 100 parts by weight



- 2 -



of CuO, additionally comprises 2 to 80, in particular 4 to 60, preferably 5 to 35 parts by weight of a water-insoluble support, in particular SiO₂ such as kieselguhr or silica gel, and/or Al₂O₃, preferably Al₂O₃.

7. The process as claimed in one or more of claims 1 to 6, wherein esters or fatty acids are reacted at from 200 to 350, in particular at from 220 to 330, preferably at from 230 to 320°C, and at from 15 to 40, in particular at from 18 to 35, preferably at from 20 to 32 MPa.

8. The process as claimed in one or more of claims 1 to 7, wherein esters of carboxylic acids, in particular of naturally occurring carboxylic acids, having from 8 to 30, in particular from 10 to 24, preferably from 12 to 22 carbon atoms, are reacted.

9. The process as claimed in one or more of claims 1 to 7, wherein fatty acids having from 8 to 30, in particular from 10 to 24, preferably from 12 to 22 carbon atoms, are reacted.

10. The process as claimed in one or more of claims 1 to 6, wherein nitriles are reacted at from 160 to 250, in particular at from 190 to 240, preferably at from 210 to 230°C, and at from 0.5 to 10, in particular at from 1.0 to 5.0, preferably at from 1.2 to 3.0 MPa.

11. The process as claimed in one or more of claims 1 to 6 and 10, wherein nitriles having from 4 to 30, in particular from 8 to 24, preferably from 10 to 22 carbon atoms, are reacted.

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