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(54) **CATALYSEUR POUR LA DESHYDROGENATION DU  
CYCLOHEXANOL, PROCEDE DE PRODUCTION ET  
UTILISATION DUDIT CATALYSEUR**

(54) **CATALYST FOR DEHYDROGENATION OF CYCLOHEXANOL,  
PROCESS FOR THE PREPARATION OF SAID CATALYST  
AND USE THEREOF**

(57) Catalyseur contenant en tant que matériau de support un .alpha.-oxyde d'aluminium et en tant que composant actif, du cuivre. La surface BET (déterminée conformément à la norme DIN 66131) de l'oxyde d'aluminium est égale ou supérieure à 30 m<sup>2</sup>/g. L'invention concerne également un procédé de production de ce catalyseur et l'utilisation de ce dernier pour la déshydrogénation du cyclohexanol en cyclohexanone. L'invention porte en outre sur l'utilisation d'.alpha.-oxyde d'aluminium dont la surface BET (selon DIN 66131) est égale ou supérieure à 30 m<sup>2</sup>/g, pour la production d'un catalyseur.

(57) The invention relates to a catalyst comprising .alpha.-aluminium oxide as the support material and copper as the active constituent, the BET surface (as defined in DIN 66131) of the aluminium oxide being not lower than 30 m<sup>2</sup>/g. It also relates to a process for preparing said catalyst according to the invention, and the use thereof in dehydrogenation of cyclohexanol to form cyclohexanone, and also to the use of .alpha.-aluminium oxide, the BET surface (as defined in DIN 66131) of said aluminium oxide being not lower than 30 m<sup>2</sup>/g, to prepare a catalyst.





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<p>(21) Internationales Aktenzeichen: <b>PCT/EP97/03135</b></p> <p>(22) Internationales Anmeldedatum: <b>17. Juni 1997 (17.06.97)</b></p> <p>(30) Prioritätsdaten:  <b>196 26 587.8      2. Juli 1996 (02.07.96)      DE</b></p> <p>(71) Anmelder (für alle Bestimmungsstaaten ausser US): <b>BASF AKTIENGESELLSCHAFT [DE/DE]; D-67056 Ludwigshafen (DE).</b></p> <p>(72) Erfinder; und  <b>(75) Erfinder/Anmelder (nur für US): HEINEKE, Daniel [DE/DE]; Lindenstrasse 24, D-67065 Ludwigshafen (DE). MEISSNER, Ruprecht [DE/DE]; Johann-Georg-Lehmann-Strasse 8, D-67273 Weisenheim (DE). HESSE, Michael [DE/DE]; Weinbietstrasse 10, D-67549 Worms (DE). MÄRKL, Robert [DE/DE]; Bolander Weg 23, D-67136 Fußgönheim (DE).</b></p> <p>(74) Gemeinsamer Vertreter: <b>BASF AKTIENGESELLSCHAFT; D-67056 Ludwigshafen (DE).</b></p>	<p>(81) Bestimmungsstaaten: <b>AL, AU, BG, BR, CA, CN, CZ, GE, HU, IL, JP, KR, LT, LV, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TR, UA, US, eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</b></p> <p><b>Veröffentlicht</b>  <i>Mit internationalem Recherchenbericht.</i></p> <p style="text-align: right; font-family: cursive; font-size: 1.2em;">47046 060108</p>	
<p>(54) Title: <b>CATALYST FOR DEHYDROGENATION OF CYCLOHEXANOL, PROCESS FOR THE PREPARATION OF SAID CATALYST AND USE THEREOF</b></p> <p>(54) Bezeichnung: <b>KATALYSATOR ZUR DEHYDRIERUNG VON CYCLOHEXANOL, VERFAHREN ZUR HERSTELLUNG DES KATALYSATORS UND VERWENDUNG DES KATALYSATORS</b></p> <p>(57) Abstract</p> <p>The invention relates to a catalyst comprising <math>\alpha</math>-aluminium oxide as the support material and copper as the active constituent, the BET surface (as defined in DIN 66131) of the aluminium oxide being not lower than 30 m<sup>2</sup>/g. It also relates to a process for preparing said catalyst according to the invention, and the use thereof in dehydrogenation of cyclohexanol to form cyclohexanone, and also to the use of <math>\alpha</math>-aluminium oxide, the BET surface (as defined in DIN 66131) of said aluminium oxide being not lower than 30 m<sup>2</sup>/g, to prepare a catalyst.</p> <p>(57) Zusammenfassung</p> <p>Katalysator, bestehend aus <math>\alpha</math>-Aluminiumoxid als Trägermaterial und Kupfer als Aktivkomponente, wobei die BET-Oberfläche (gemessen nach DIN 66131) des Aluminiumoxids nicht kleiner als 30 m<sup>2</sup>/g ist sowie Verfahren zur Herstellung des erfindungsgemäßen Katalysators sowie dessen Verwendung bei der Dehydrierung von Cyclohexanol zu Cyclohexanon und die Verwendung von <math>\alpha</math>-Aluminiumoxid mit einer BET-Oberfläche (gemessen nach DIN 66131) des Aluminiumoxids von nicht kleiner als 30 m<sup>2</sup>/g zur Herstellung eines Katalysators.</p>		

Catalyst for dehydrogenation of cyclohexanol, process for the preparation of said catalyst and use thereof

Description

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The present invention relates to an improved copper on  $\alpha$ -alumina catalyst wherein the BET surface area (measured according to DIN 66131) of the alumina is not less than 30 m<sup>2</sup>/g.

- 10 This invention further relates to a process for preparing the catalyst of this invention and to its use in the dehydrogenation of cyclohexanol to cyclohexanone and to the use of an  $\alpha$ -alumina having a BET surface area (determined according to DIN 66131) of not less than 30 m<sup>2</sup>/g for preparing a catalyst.

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Cyclohexanone is an important intermediate for nylon-6 and nylon-6,6 and is largely produced in industry by catalytic dehydrogenation of cyclohexanol. There are two versions of the process for the catalytic dehydrogenation of cyclohexanol. The high

- 20 temperature version is carried out at from 320 to 420°C, the low temperature version at from 220 to 260°C.

The high temperature dehydrogenation has the disadvantage of low cyclohexanol selectivities, since appreciable side-reactions take place at the high temperatures, such as the dehydration of cyclohexanol to cyclohexene or dimerizations such as the formation of cyclohexanylcyclohexanone. The by-products necessitate an extensive workup and impair the economics of the process.

- 25 place at the high temperatures, such as the dehydration of cyclohexanol to cyclohexene or dimerizations such as the formation of cyclohexanylcyclohexanone. The by-products necessitate an extensive workup and impair the economics of the process.
- 30 The low temperature dehydrogenation of cyclohexanol is catalyzed with copper-based catalysts in particular. These catalysts make it possible to lower the reaction temperature to about 240-280°C and hence give higher cyclohexanone selectivities. However, because the equilibrium is displaced at the comparatively low temperature, the conversions are generally not very high.

- 35 perature, the conversions are generally not very high.
- One class of these low temperature catalysts comprises compositions of copper and a ceramic support, which can be SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> or a mixture thereof. The copper content of these catalysts can be up to 50% by weight. These catalysts may further comprise small amounts of alkali metals as promoters.

- 40 be up to 50% by weight. These catalysts may further comprise small amounts of alkali metals as promoters.
- For instance, GB-A 1081491 discloses Cu/Al<sub>2</sub>O<sub>3</sub>, SU-A 465217 discloses Cu/Li/SiO<sub>2</sub> and SU-A 522853 discloses Cu/K/Al<sub>2</sub>O<sub>3</sub> for the nonoxidative dehydrogenation of cyclohexanol. The copper catalysts in question are usually prepared by applying the active copper component either to a prefabricated support, by precipita-

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tion of a copper salt or by impregnation with a suitable copper salt solution, or by coprecipitating the components making up the catalyst. A further way of preparing copper catalysts is to dry mix the components and then calcine the mixture.

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Electroless coppering or reductive precipitation of the copper on a support using a reductant in the presence of a complexing agent to prepare copper catalysts for the nonoxidative dehydrogenation of cyclohexanol is known from Chang et al., Appl. Catal. A 103 (1994) 233-42. The support used is an  $\alpha$ - $\text{Al}_2\text{O}_3$  having a surface area of 22.6  $\text{m}^2/\text{g}$ . According to Chang, the selectivity is affected by the acidity of the support in that acidic supports such as  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  will catalyze side-reactions such as the dehydration to cyclohexene or dimerizations. By adding alkali metal or alkali earth metal ions it is possible to reduce the acidity (see for example Appl. Cat. A: General Vol. 83, No. 2 (1992), 201-11), but this measure will also reduce the activity. The advantage of higher activity for copper catalysts over high temperature catalysts is thus lost again to some extent by alkali metal or alkali earth metal doping.

The catalysts described in Appl. Catal. A 103 (1994) 233-42, however, are not suitable for industrial application, since they are powders. Pressing into shaped articles such as tablets is difficult because of the poor tabletability. In addition, the low hardness of the resulting shaped articles is responsible for a low attrition resistance in the reactor, resulting in an increasing pressure drop as the reaction proceeds. Thus, full-scale use in industry is generally not possible.

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A further disadvantage of using  $\alpha$ - $\text{Al}_2\text{O}_3$  as support material is the low interaction with the active copper component. This low interaction is responsible for rapid agglomeration of the active component, resulting in a loss of catalytically active surface area and hence decreased activity. To achieve high conversions none the less, the reactor temperature would have to be raised in the course of the dehydrogenation, which, however, would further accelerate the agglomeration and the attendant deactivation of the catalyst.

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It is an object of the present invention to provide a catalyst which does not have the aforementioned disadvantages. More particularly, the catalyst shall have a long on-stream life and dehydrogenate cyclohexanol to cyclohexanone in high yield and high selectivity at comparatively low reaction temperatures. Constant readjustment of the reaction temperature shall likewise be unnecessary. In addition, the catalyst shall be readily processible

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into shaped articles, especially into tablets, strands, rings, cylinders, and shall also be usable in that form because of good hardness and attrition resistance.

- 5 We have found that this object is achieved by an improved copper on  $\alpha$ -alumina catalyst, wherein the BET surface area (measured according to DIN 66131) of the alumina is not less than 30 m<sup>2</sup>/g.

This invention further provides a process for preparing the catalyst of this invention, its use in the dehydrogenation of cyclohexanol to cyclohexanone and the use of an  $\alpha$ -alumina having a BET surface area (measured according to DIN 66131) of not less than 30 m<sup>2</sup>/g for preparing a catalyst.

- 15 The catalyst of this invention is prepared by applying the active copper component in a conventional manner, such as impregnating, precipitating, dry mixing or electroless coppering, to an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> support having a BET surface area of not less than 30 m<sup>2</sup>/g.

- 20 The  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> used preferably has a BET surface area within the range from 50 to 300 m<sup>2</sup>/g, particularly preferably within the range from 100 to 250 m<sup>2</sup>/g. Such high-BET  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is commercially available (for example from Alcoa).

- 25 Impregnation generally comprises saturating the support with an aqueous solution of copper salts, preferably with the nitrates, sulfates, acetates or chlorides of copper, drying and then calcining the impregnated support.

- 30 Precipitation customarily comprises admixing an aqueous solution of a copper salt (see above) in the presence of the support with a precipitant which will lead to the formation of a sparingly soluble copper compound. Sodium carbonate is preferred for precipitating the copper. This is followed by drying and calcining  
35 in a conventional manner.

Dry mixing generally comprises mixing the support with the desired copper salt and then calcining.

- 40 In a further preferred embodiment, the catalyst is prepared by electroless deposition (coppering) in the presence of the high-BET  $\alpha$ -alumina used herein (see also Appl. Catal. A 103 (1994) 233-242). To this end, the support is generally first seeded with a noble metal such as platinum, rhodium, iridium, gold or palla-  
45 dium, preferably palladium, to form crystallization-initiating centers. A copper complex is then treated with a reductant to deposit the copper on the support.

To prevent premature precipitation of the copper at the usually high pH required, it is preferable to add a strong complexing agent such as ethylenediaminetetraacetate, its alkali metal salts  
5 such as the tetrasodium salt, ethylenediamine or phenanthroline. The reduction (or the actual coppering) is then generally effected using a reductant capable of depositing copper(0) from copper salt solutions, such as formaldehyde or sodium formate.

10 From observations to date, we think that electroless deposition produces particularly small copper particles. Their size is generally below 50 nm, preferably below 20 nm, as measured by X-ray diffraction.

15 Regardless of the manner of applying the copper to the support, the resulting powder, or the corresponding shaped article, is calcined at a temperature within the range from 250 to 450°C in air or in an inert gas atmosphere, advantageously in nitrogen, for a period ranging from 1 to 24 h. Shaped articles can be  
20 formed before or after the calcining.

The catalyst powder obtained from electroless deposition or from the other processes recited above is preferably compacted into shaped articles such as tablets, strands, rings, wagon wheels,  
25 stars, monoliths, balls, granules or extrudates, preferably tablets, generally by admixture of tableting aids. The customary tableting aids can be used. Examples are graphite, magnesium stearate, methylcelluloses (such as Walocel®), copper powder or mixtures thereof.

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The copper content of the catalyst will customarily be within the range from 0.01 to 50% by weight, preferably within the range from 2 to 30% by weight, particularly preferably within the range from 5 to 20% by weight, based on the total weight of the cata-  
35 lyst material.

The BET surface area (measured according to DIN 66131) of the catalyst is generally not below 30 m<sup>2</sup>/g, preferably within the range from 50 to 300 m<sup>2</sup>/g, particularly preferably within the  
40 range from 100 to 250 m<sup>2</sup>/g.

The dehydrogenation of cyclohexanol to cyclohexanone is generally carried out in the gas phase at from 180 to 400°C, preferably at from 200 to 350°C, particularly preferably at from 220 to 260°C.  
45 The pressure will generally be within the range from 50 kPa to 5 MPa; atmospheric pressure is employed in particular.

## 5

The starting material for the reaction will generally be a mixture of cyclohexanol and cyclohexanone. It is of course also possible to use pure cyclohexanol. The mixture used will customarily comprise from 50 to 100, preferably from 60 to 99, in particular 5 96, % by weight of cyclohexanol and from 50 to 0, preferably from 40 to 1, especially 4, % by weight of cyclohexanone. Cyclohexanone and cyclohexanol are customarily obtained by oxidation of cyclohexane and subsequent concentrating of the cyclohexanol by distillative removal of cyclohexanone and other low boilers.

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In general, the catalyst is reduced with hydrogen before the actual reaction. This is generally done by passing a hydrogen stream diluted with an inert gas, preferably nitrogen, over the catalyst at a certain temperature, preferably within the range 15 from 120 to 300°C. The hydrogen content of the reducing gas is then customarily increased continuously until there is no further significant change in the temperature.

In a preferred embodiment, the starting material is passed as a 20 gas over the catalyst at a liquid hourly space velocity (LHSV) of preferably from 0.1 to 100 h<sup>-1</sup>, particularly preferably of from 0.1 to 20 h<sup>-1</sup>. The starting material can be mixed with an inert gas such as nitrogen or with steam. The dehydrogenation product can be worked up in a conventional manner (see for example DE-A 25 1,296,625 and DE-A 1,443,462) for further processing.

In a further preferred embodiment, hydrogen is separated from the reaction mixture leaving the reaction zone and added to the gas mixture entering the reaction zone. It is further advantageous to 30 recycle the reaction mixture until the desired conversion is achieved.

The catalyst of this invention is very active and can therefore be operated at significantly lower temperatures than catalysts 35 currently used in industry, is quick to activate and gives high selectivities and conversions close to the equilibrium. In addition, noticeable deactivation occurs only after distinctly longer periods than hitherto customary with existing catalysts.

40 The catalyst of this invention is notable for good tabletability, adequate hardness, high conversions at low operating temperatures, high cyclohexanone selectivities and a long on-stream life.

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## Examples

## Example 1 - Catalyst preparation

5 5 g of polyvinylpyrrolidone ("PVP", from Merck, Order No. 7443, average molar mass 25,000 g/mol) were added to a mixture of 27.27 g of an 11% strength by weight  $\text{Pd}(\text{NO}_3)_2$  solution (calculated as Pd), 495 ml of bidistilled water and 495 ml of ethanol, and the resulting mixture was refluxed for 4 h. The resulting sol 10 ("Pd sol") had a palladium content of 0.34% by weight (based on the total weight of the Pd sol).

20.6 ml of the above-prepared Pd sol were admixed with 23 ml of water and 125 g of  $\alpha\text{-Al}_2\text{O}_3$  (from Alcoa, BET surface area 156  $\text{m}^2/\text{g}$ , 15 water uptake 0.35 ml/g of  $\text{Al}_2\text{O}_3$ ). The saturated support was then air dried. The pretreated and dried support was suspended in 3,894 ml of a freshly prepared solution which was 0.1 M in  $\text{Cu}(\text{OAc})_2$ , 0.2 M in  $\text{Na}_4\text{EDTA}$ , 0.2 M in formaldehyde and 0.0125 M in pyridine. A pH of 12.5 was set with 35% strength by weight NaOH 20 and vigorous stirring. A grayish black to reddish brown color was observed. The suspension was heated to 70°C and the pH was maintained within the range from 12 to 12.5 with further NaOH (NaOH consumption: about 400 ml). The suspension was stirred at 70°C for 30 min and then cooled down to room temperature. The suspension 25 was filtered and the filter residue was washed neutral with water (filtrate had a slightly blue color). The washed solid was then dried at 110°C under nitrogen for 16 h and subsequently calcined at 300°C for 2 h.

30 The resulting catalyst contained 16.5% by weight of copper and 0.046% by weight of sodium, based on the total weight of the grayish black catalyst.

An XRD determination of the crystalline constituents yielded the 35 following data:  $\text{Al}_2\text{O}_3$  (19 nm);  $\text{CuO}$  (13.0 nm),  $\text{Cu}_2\text{O}$  (traces).

Forming of tablets (5 mm in length, 3 mm in diameter)

100 g of the above-prepared catalyst powder were precompact 40 with 1% by weight of copper powder "FFL" (Norddeutsche Affinerie # 10914) and 1% by weight of magnesium stearate (Riedel de Haën # 4162757), each based on the catalyst weight, to form tablets 20 mm in length and 1 mm in diameter. These tablets were then forced through a screen having a mesh size of 1.6 mm and, follow- 45 ing the addition of 2% by weight of graphite, press molded into tablets 5 mm in length and 3 mm in diameter.



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The side crushing strength of the tablets was 53 N with a standard deviation of 16 N (measured using an instrument from Frank, Model No. 81557).

## 5 Example 2 - Catalyst test

The catalyst tests were carried out in a tubular reactor 5 cm in diameter and 60 cm in length. For each test, 200 ml of the catalyst were installed and activated with hydrogen before the reaction. Before the starting material was introduced, the catalyst was activated with 150 l of N<sub>2</sub>/h and 1.5 l of H<sub>2</sub>/h at 120°C. The hydrogen stream was stopped as soon as the temperature rose by more than 10°C. The temperature was then raised in 20°C increments to 240°C while the hydrogen rate was kept constant. At 240°C the catalyst was then activated with 150 l of N<sub>2</sub>/h and 7.5 l of H<sub>2</sub>/h. After activation, the catalyst was subjected to a 96% cyclohexanol/4% cyclohexanone mixture at an LHSV of about 0.7 h<sup>-1</sup>. The reactor effluents were analyzed by gas chromatography. The results are given in the table below.

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Comparative example:

The dehydrogenation test of Example 2 was repeated using a commercial copper catalyst (catalyst CU 940 from Procatalyse).

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Catalyst	Temperature [°C]	Time [h]	Conversion [%]	Selectivity [%]
Example 2	229	42	57	97.7
	228	150	56	99.2
	228	246	59	99.4
	226	438	55	99.9
	229	558	55	99.7
	237	630	61	99.6
	242	774	60	99.5
Comparison	277	0	68	98.3
	275	12	63	98.4
	275	24	62	98.5
	275	36	61	98.6
	276	48	61	98.5
	280	168	60	98.1

The catalyst of this invention gives a conversion close to the equilibrium at a very high selectivity of >99% at as low as >230°C. No noticeable deactivation of the catalyst took place at this temperature. By slightly raising the reaction temperature to about 240°C, the conversion can be increased to about 60% without loss of selectivity. At this temperature too deactivation was again very gradual.

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As can be seen, the comparative test required a temperature adjustment after just 168 h to maintain the conversion, whereas such a correction was not necessary with the catalyst prepared according to this invention until after about 600 h. In addition, the temperatures of the comparative example are about 40°C above the temperatures of the representative example. Finally, the selectivities of the representative example are optimal. This was unforeseeable for an alumina having a BET surface area of not less than 30 m<sup>2</sup>/g.

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We claim:

1. A copper on  $\alpha$ -alumina catalyst wherein the BET surface area  
5 (measured according to DIN 66131) of the alumina is not less than 30 m<sup>2</sup>/g.
2. A copper on  $\alpha$ -alumina catalyst wherein the BET surface area  
10 (measured according to DIN 66131) of the alumina is not less than 30 m<sup>2</sup>/g, obtainable by applying copper to the  $\alpha$ -alumina support material in a conventional manner by impregnating, precipitating, dry mixing or electroless coppering.
3. A process for preparing a catalyst as claimed in claim 1 or 2  
15 by applying copper to an  $\alpha$ -alumina support material in a conventional manner by impregnating, precipitating, dry mixing or electroless coppering, which comprises using an  $\alpha$ -alumina having a BET surface area (determined according to DIN 66131) of not less than 30 m<sup>2</sup>/g.  
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4. A process as claimed in claim 3, further comprising processing the catalyst into shaped articles, especially into tablets, strands, rings, cylinders.
- 25 5. The use of a catalyst as claimed in claim 1 or 2 or prepared as claimed in claim 3 or 4 for preparing cyclohexanone by dehydrogenation of cyclohexanol.
6. The use of an  $\alpha$ -alumina having a BET surface area (determined  
30 according to DIN 66131) of not less than 30 m<sup>2</sup>/g for preparing a catalyst.

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