

Dehydrogenation of secondary cyclic alcohols

The present invention relates to a process for dehydrogenating
5 secondary alcohols in the presence of a catalyst comprising zinc
oxide and calcium carbonate at elevated temperature in the gas
phase.

DE-A 1,443,462 discloses a process for dehydrogenating primary
10 and secondary alcohols in which the alcohol used is
dehydrogenated at elevated temperature in the gas phase over
catalysts consisting predominantly of zinc oxide to give the
corresponding aldehyde or ketone. The catalyst can contain both
15 copper compounds and alkaline earth metals. During the
dehydrogenation, ie. after hydrogen elimination has commenced,
the hydrogen feed in the process described is discontinued. In
particular, the dehydrogenation of cyclohexanol to cyclohexanone
is described, but the yield of cyclohexanone is only 81.5 %.
Apart from 17 % of unreacted cyclohexanol, the reaction mixture
20 contains from 0.1 to 0.5 % of hydrocarbons and 1 % of
higher-boiling condensation products.

DE-B 1,296,625 describes a process for preparing cyclohexanone
from cyclohexanol contaminated with organic acids and esters at
25 elevated temperatures in the presence of a zinc-containing
catalyst comprising zinc oxide-zinc carbonate or mixtures of zinc
oxide-zinc carbonate with calcium oxide-calcium carbonate or with
magnesium oxide-magnesium carbonate. A disadvantage of this
process is the excessive decrease in the pellet hardness in
30 long-term operation which leads to frequent replacement of the
catalyst and corresponding down times. The decrease in the pellet
hardness in long-term operation results from the massive
decomposition of the carbonates by organic acids or from phase
transformations.

35 Acta Chim. Acad. Sci. Hung 107 (1981) 343-360, Acta Chim. Acad.
Sci. Hung 97 (1978) 439-449 disclose that in the dehydrogenation
of cyclohexanol in the presence of hydrogen and catalysts
comprising elements of the eighth transition group, e.g. rhodium,
40 nickel and platinum, increased amounts of cracking products and
formation of phenol and benzene are observed in comparison with
processes not using hydrogen. This is not observed in the
dehydrogenation of aliphatic alcohols: thus DE-A 2,028,350
describes a process for dehydrogenating [sic] aldehydes and
45 ketones, in particular for preparing acetone and methyl isobutyl
ketone, over a copper-containing catalyst in the presence of
hydrogen. It may be remarked that although this reference

mentions cyclohexanol as starting material among many others, there are no experimental data on the dehydrogenation of cyclohexanol. In all probability it would also be possible to prepare cyclohexanone by the process described in DE-A 2,028,350, 5 but in the light of the abovementioned Acta Chim. Acad. Sci. Hung 107 (1981) 343-360 and also Acta Chim. Acad. Sci. Hung 97 (1978) 439-449 one would have to expect by-products which prohibit economical use.

10 It is an object of the present invention to provide a process in which cyclic ketones, in particular cyclohexanone, can be obtained in higher selectivities and yields than hitherto possible and in which the formation of cracking products and aromatic by-products is minimized. The present invention is also 15 to make available a catalyst which in long-term operation has a good pellet hardness, particularly in respect of compressive strength on the end face and lateral compressive strength, so that the catalyst has to be replaced less often than hitherto.

20 We have found that this object is achieved by a process for dehydrogenating secondary alcohols in the presence of a catalyst comprising zinc oxide and calcium carbonate at elevated temperature in the gas phase, wherein secondary cyclic alcohols are used and the dehydrogenation is carried out in the presence 25 of hydrogen and a catalyst whose active components comprise from 30 to 60 % by weight of zinc oxide and from 40 to 70 % by weight of calcium carbonate in the calcite modification.

In addition, a dehydrogenation catalyst and a process for its 30 preparation and its use have been found.

Secondary alcohols which can be used according to the present invention are cycloaliphatic alcohols having from 5 to 16 carbon atoms, for example cyclopentanol, cyclohexanol, 35 4-methylcyclohexanol, cyclooctanol, cyclododecanol and cyclohexadecanol, preferably cyclohexanol.

The zinc oxide-containing catalyst used according to the present invention is a catalyst whose active components comprise from 30 40 to 60 % by weight, preferably from 40 to 50 % by weight, of zinc oxide and from 40 to 70 % by weight, preferably from 50 to 60 % by weight, of calcium carbonate in the calcite modification.

In a preferred embodiment, the catalyst of the present invention 45 has a BET specific surface area of from 5 to 50 m²/g, preferably from 10 to 30 m²/g.

Such a catalyst is obtainable according to the present invention by precipitation of sparingly soluble zinc and calcium compounds from water-soluble zinc and calcium compounds using a base and subsequent work-up in a manner known per se, wherein

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(a) the base used is a water-soluble basic carbonate,

(b) if desired, the sparingly soluble zinc and calcium compounds are filtered off after precipitation,

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(c) the zinc and calcium compounds, which may have been filtered off, are washed,

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(d) the washed zinc and calcium compounds from (c) are dried to give a powder, and subsequently

(e) the powder from (d) is calcined at not above 600°C, and

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(f) if desired, the calcined powder is pressed to give shaped bodies.

Water-soluble zinc and calcium salts which can be used are acetates, sulfates, nitrates, preferably nitrates such as zinc nitrate, zinc acetate, zinc sulfate, calcium acetate, calcium
25 nitrate, preferably zinc nitrate and calcium nitrate. The aqueous solutions of the appropriate salts usually have concentrations in the range from 3 to 25 % by weight, preferably from 10 to 25 % by weight, in particular 20 % by weight.

30 The molar ratio of zinc to calcium is selected such that after calcination the active components of the catalyst comprise from 30 to 60 % by weight of zinc oxide and from 40 to 70 % by weight of calcium carbonate in the calcite modification.

35 Bases used are water-soluble basic carbonates such as alkali metal carbonates, e.g. sodium carbonate, potassium carbonate, alkali metal hydrogen carbonates, e.g. sodium hydrogen carbonate, potassium hydrogen carbonate, ammonium carbonate or ammonium hydrogen carbonate and mixtures thereof, preferably sodium
40 carbonate, particularly preferably in the form of its aqueous solutions generally having concentrations in the range from 0.5 to 30, preferably from 10 to 25, gram of base/100 gram of solution.

45 The precipitation is generally carried out at from 10 to 90°C, preferably from 40 to 80°C. After the precipitation, the precipitate can be filtered off if desired. The precipitate,

which may have been filtered off, is generally washed with water, preferably until nitrate can no longer be detected by means of the nitrate ring test, and is subsequently dried at preferably from 90 to 150°C to give a dry powder. Drying can be carried out
5 in a static or moving bed, preferably by spray drying.

According to the present invention, the dried powder is calcined at not above 600°C, preferably in the range from 300 to 600°C, in particular from 400 to 475°C, preferably in air. According to
10 observations up to now, prolonged heating at above 600°C leads to the formation of the aragonite modification of CaCO_3 . Brief heating to above 600°C is not detrimental to the preparation of the catalysts of the present invention, as long as no aragonite is formed (ie. cannot be detected by means of X-ray
15 diffractometry).

After calcination, the calcined powder can, if desired, be pressed to give shaped bodies such as pellets, rings, cylinders, etc., preferably pellets.

20 In a preferred embodiment, the calcined powder is pressed together with graphite, preferably with from 0.1 to 5 % by weight, particularly preferably from 1 to 2.5 % by weight, in particular 2 % by weight, of graphite, based on the total mass.

25 In a further preferred embodiment, the uncalcined powder from step (c) (see above) is pressed to form shaped bodies, preferably to form pellets, and the shaped bodies thus obtained are calcined as described under step (d).

30 The calcined powders and shaped bodies thus obtained can be used as catalysts, these catalysts containing zinc oxide and calcium carbonate (in the calcite modification) as active components and, if desired, graphite as passive component.

35 The catalysts of the present invention have the following physical properties:

In a further preferred embodiment, the catalyst of the type
40 claimed in the present invention has a pore volume in the range from 0.10 to 0.50 cm^3/g , in particular from 0.20 to 0.35 cm^3/g , at a pore diameter in the range from 5 nm to 300 μm , where particularly preferably at least 85 %, preferably more than 90 %, of this pore volume is associated with a pore diameter in the
45 range from 0.01 to 0.5 μm .

Particularly preferred catalysts of the type mentioned are those which have a compressive strength on the end face in the range from 500 to 4000 N/cm², in particular from 1000 to 2500 N/cm² and a lateral compressive strength of from 30 to 300 N, preferably from 50 to 200 N. These values can also be achieved without calcination. The important thing is that these strength ranges are retained under operating conditions (reaction conditions). However, this is only the case if no phase transformations occur. This condition is met by the process of the present invention.

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The BET specific surface area is generally from 5 to 50 m²/g, preferably from 10 to 30 m²/g. The pore volume in the pore diameter range from 5 nm to 300 μm is usually from 0.1 to 0.5 cm³/g, preferably from 0.2 to 0.35 cm³/g, with the proviso that at least 85 %, preferably more than 90 %, of this pore volume is in the pore diameter range from 0.01 to 0.5 μm.

The compressive strength on the end face of the pellets is preferably from 500 to 4000 N/cm², in particular from 1000 to 2500 N/cm² and the lateral compressive strength of the pellets is preferably from 30 to 300 N, preferably from 50 to 200 N.

In a particularly preferred embodiment, the precipitate of sparingly soluble zinc and calcium compounds, preferably zinc hydroxide carbonate and calcium carbonate, is washed on filter presses, the filter cake thus obtained is slurried with water and the slurry is dried by spraying in a spray dryer. The spray-dried powder obtained in this way can then be further processed as described above.

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According to the present invention, the gaseous secondary, cyclic alcohol, preferably cyclohexanol, into which from 1 to 20 % by volume, preferably from 5 to 10 % by volume, of hydrogen, based on the amount of alcohol, has been mixed is brought into contact with the catalyst used in a manner customary per se, for example in a fixed-bed reactor or in a fluidized-bed reactor, preferably in a tube reactor in which the catalyst is arranged as a fixed bed. The product mixture is usually worked up by distillation.

In general, the alcohol to be used is vaporized in a manner known per se, for example in a vaporizer, and the desired amount of gaseous hydrogen is then mixed in.

The temperature of the gas phase in the reaction zone is usually selected so as to be in the range from 200 to 500°C, preferably from 300 to 450°C. In a preferred embodiment, the temperature range is selected such that a conversion in the range from 50 to

90 %, preferably from 65 to 75 %, of alcohol is obtained. In the case of cyclohexanol as starting compound, the temperature is selected so as to be in the range from 350 to 400°C.

- 5 The pressure of the gas phase in the reaction zone is generally selected so as to be in the range from 80 to 4000 kPa, preferably from 100 to 1000 kPa.

The space velocity over the catalyst is generally selected so as
10 to be in the range from 0.5 to 3.0, preferably from 0.6 to 2.0, liters of alcohol per liter of catalyst per hour.

In a preferred embodiment, the hydrogen is separated from the reaction mixture leaving the reaction zone and is added to the
15 gas mixture entering the reaction zone.

The ketones such as cyclohexanone prepared according to the present invention are important large-scale industrial products. For example, cyclohexanone is customarily further used,
20 preferably in the resulting mixture with cyclohexanol, for preparing adipic acid.

The advantage of the process of the present invention is that cyclic ketones, in particular cyclohexanone, can be obtained in
25 higher yields than hitherto possible, and the formation of cracking products and aromatic by-products is minimized.

Examples

- 30 Example 1: preparation of a calcined catalyst (Cl₀)

For the preparation of the catalyst, two solutions are required. Solution 1 is an aqueous solution of zinc nitrate and calcium nitrate having a concentration of 20 % by weight in which the
35 molar ratio of zinc:calcium = 1:1.6. Solution 2 is a 2M aqueous sodium carbonate solution.

Both solutions are heated to 70°C and pumped in parallel into a precipitation vessel. The feed rate of the solutions is regulated
40 such that a pH of 7.8 ± 1.0 is maintained during the precipitation. The precipitate obtained in this parallel precipitation is filtered off and washed with water until nitrate can no longer be detected (test using FeSO₄ solution and concentrated H₂SO₄, known as the nitrate ring test). The precipitate is subsequently
45 slurried in water and spray dried. The powder thus obtained is heated in air for 5 hours at 450°C and, after cooling and addition

of 2 % by weight of graphite, pressed to give 5x5 mm pellets. The physical data for the catalyst ("Cl₀") are shown in Table 1.

Example 2: dehydrogenation using Cl₀

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920 g of the catalyst Cl₀ prepared as described in Example 1 were installed in a tube reactor having a length of 0.6 m and an internal diameter of 0.05 m. Via a vaporizer, 640 ml/h of liquid cyclohexanol were fed in gaseous form into the reactor. 7 l/h of hydrogen were metered in upstream of the reactor. The temperature of the reaction mixture in the reaction zone was maintained at 331°C. At this temperature, the conversion based on cyclohexanol used was 70 %. The reaction mixture leaving the reactor was cooled to room temperature with release of hydrogen. The liquid reaction products were analyzed by gas chromatography. At a conversion of 70 %, a selectivity of 99.0 % and a residue of 0.70 % were obtained after 1800 hours. The catalyst (Cl₁₈₀₀) had the physical properties shown in Table 1.

20 Comparative Example 1 - Preparation of an uncalcined catalyst and dehydrogenation therewith

Calcium carbonate and zinc hydroxide carbonate were precipitated from an aqueous zinc and calcium nitrate solution by means of 2M sodium carbonate solution, as described in Example 1. The precipitate was washed free of nitrate and after slurring with H₂O was spray dried. The dry powder thus obtained was, after addition of 2 % by weight of graphite, pressed to give 5 x 5 mm pellets. The catalyst thus obtained ("C2₀") has the physical properties indicated in Table 1. X-ray analysis shows calcite as main component and aragonite and zinc hydroxide carbonate as secondary components. 920 g of this catalyst were, as described in Example 2, tested at a cyclohexanol conversion of 70 %. After 1800 hours, the selectivity of the catalyst was 98.5 % and the amount of residue formed was 0.88 %. The catalyst (C2₁₈₀₀) had the physical properties indicated in Table 1.

Example 3: dehydrogenation using Cl₀ (140 h)

40 920 g of the catalyst (Cl₀) prepared as described in Example 1 were installed in a tube reactor having a length of 0.6 m and an internal diameter of 0.05 m. Via a vaporizer, 640 ml/h of liquid cyclohexanol were fed in gaseous form into the reactor. 7 l/h of hydrogen were metered in upstream of the reactor. The temperature in the reaction zone was maintained at 341°C. At this temperature, the conversion based on cyclohexanol used was 70 %. The reaction mixture leaving the reactor was cooled to room temperature with

release of hydrogen. The liquid reaction products were analyzed by gas chromatography. At a conversion of 70 %, a selectivity of 98.7 % and a residue of 0.80 % were obtained after 140 hours. The catalyst was removed from the reactor (C1₁₄₀) and had the physical properties indicated in Table 1.

Comparative Example 2: dehydrogenation using C2₀, without hydrogen

Example 3 was repeated using catalyst (C2₀) from Comparative Example 1 with the further differences that no hydrogen was used, the reaction temperature was 323°C and the duration of the experiment was 143 hours. At a conversion of 70 %, the selectivity based on cyclohexanol used was 96.6 % and the residue was 2.37 %. The catalyst removed from the reactor (C2₁₄₃) had the physical properties indicated in Table 1.

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Table 1

Physical data for the catalysts

Example No.	BET surface area [m ² /g]	Total pore volume in the range from 0.005 to 300 μ m pore diameter [m ³ /g]	Pore volume in the pore diameter range from 0.01 to 0.5 μ m [%]	Compressive strength on the end face N/cm ²	Lateral compressive strength [N]	Phases by X-ray analysis	Operating time [h]
1(C1 ₀)	14.6	0.23	96.8	1947	94	CaCO ₃ calcite (main component) ZnO (secondary component) C graphite	0
2(C1 ₁₈₀₀)	12.1	0.21	94.5	847	46	CaCO ₃ calcite (main component) CaCO ₃ aragonite (secondary component) Zn ₄ CO ₃ (OH) ₆ H ₂ O C graphite	1800
Comparative Example 1 (C2 ₀)	12.5	0.19	84.0	1807	70	CaCO ₃ calcite (main component) CaCO ₃ aragonite (secondary component) Zn ₄ CO ₃ (OH) ₆ H ₂ O C graphite	0
Comparative Example 1 (C2 ₁₈₀₀)	17.3	0.27	72.5	664	18	CaCO ₃ calcite (main component) ZnO (secondary component) CaCO ₃ aragonite (small amount) C graphite	1800

The catalyst C1₀ according to the present invention has both a higher compressive strength on the end face and a higher lateral compressive strength than the uncalcined catalyst C2₀. Furthermore the lateral compressive strength of the catalyst C1 only drops after 1800 hours to 49 % of the initial value of the lateral compressive strength, while in the case of comparative catalyst C2₁₈₀₀ containing aragonite the lateral compressive strength drops to a quarter (26 %) of the initial value, which in industrial use means more down time for replacing the aragonite-containing catalyst.

Table 2: Overview of the dehydrogenation experiments

Example	Temperature [°C]	Selectivity [%]	Amount of hydrogen added [l/h]	Conversion [%]	Residue ¹ [%]	Catalyst
2	331	99.0	7	70	0.70	C1 ₀ -->C1 ₁₈₀₀
Comparative Example 1	331	98.5	7	70	0.88	C2 ₀ -->C2 ₁₈₀₀
3	341	98.7	7	70	0.80	C1 ₀ -->C1 ₁₄₀
Comparative Example 2	323	96.6	0	70	2.37	C2 ₀ -->C2 ₁₄₃

1) Residue: based on the total mass of the liquid reaction mixture



We claim:

1. A process for dehydrogenating secondary alcohols in the presence of a catalyst comprising zinc oxide and calcium carbonate at elevated temperature in the gas phase, wherein secondary cyclic alcohols are used and the dehydrogenation is carried out in the presence of hydrogen and a catalyst whose active components comprise from 30 to 60 % by weight of zinc oxide and from 40 to 70 % by weight of calcium carbonate in the calcite modification.
2. A process as claimed in claim 1, wherein the secondary cyclic alcohol used is cyclohexanol.
3. A process as claimed in claim 1 or 2, wherein the catalyst used has a BET specific surface area in the range from 5 to 50 m²/g.
4. A process as claimed in any of claims 1 to 3, wherein the catalyst used has a pore volume at a pore diameter in the range from 5 nm to 300 μm of from 0.1 to 0.5 cm³/g.
5. A process as claimed in claim 4, wherein at least 85 % of the pore volume has a pore diameter in the range from 0.01 to 0.5 μm.
6. A dehydrogenation catalyst having the active components comprising from 30 to 60 % by weight of zinc oxide and from 40 to 70 % by weight of calcium carbonate in the calcite modification.
7. A dehydrogenation catalyst as claimed in claim 6 having a BET specific surface area in the range from 5 to 50 m²/g.
8. A dehydrogenation catalyst as claimed in claim 6 or 7 having a pore volume at a pore diameter in the range from 5 nm to 300 μm of from 0.10 to 0.50 cm³/g.
9. A dehydrogenation catalyst as claimed in claims 6, 7 or 8, wherein at least 85 % of the pore volume of the catalyst has a pore diameter in the range from 0.01 to 0.5 μm.
10. A process for preparing the dehydrogenation catalyst as claimed in claim 6 by precipitation of sparingly soluble zinc and calcium compounds from water-soluble zinc and calcium



salt solutions using a base and subsequent work-up in a manner known per se, wherein

- 5 (a) the base used is a water-soluble basic carbonate,
- (b) if desired, the sparingly soluble zinc and calcium compounds are filtered off after precipitation,
- 10 (c) the zinc and calcium compounds, which may have been filtered off, are washed,
- (d) the washed zinc and calcium compounds from (c) are dried to give a powder, and subsequently
- 15 (e) the powder from (d) is calcined at not above 600°C, and
- (f) if desired, the calcined powder is pressed to give shaped bodies.
- 20 11. A process for preparing the dehydrogenation catalyst as claimed in claim 10, wherein after step (c) and before step (d) the powder is pressed to give shaped bodies and is subsequently calcined at not above 600°C.
- 25 12. A process as claimed in claim 10, wherein the precipitate of sparingly soluble zinc and calcium compounds is washed on filter presses, the resulting filter cake is subsequently slurried with water, the slurry is then dried by spraying in a spray drier and the powder obtained is then further processed as described under (d) [sic] and, if desired, (e) [sic].
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13. Use of the dehydrogenation catalyst as claimed in any of claims 6 to 9 or prepared as claimed in any of claims 10 to 12 for the dehydrogenation of secondary cyclic alcohols.
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14. A dehydrogenation catalyst as claimed in any of claims 6 to 9 or prepared as claimed in any of claims 10 to 12, which in pellet form has a compressive strength on the end face in the range from 500 to 4000 N/cm² and a lateral compressive
- 40 strength in the range from 30 to 300 N.
15. A dehydrogenation catalyst as claimed in claim 14, wherein only calcite and zinc oxide can be detected by X-ray diffraction on the dehydrogenation catalyst.
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