

Mixed oxide catalysts for catalytic gas phase oxidation

The invention relates to mixed oxide catalysts and to their use for the catalytic gas phase oxidation of alkanes or mixtures of alkanes and olefins and to processes for
5 preparing the catalysts.

In particular, the catalyst can be used to convert propane to acrolein and acrylic acid or isobutane to methacrolein and methacrylic acid, acrolein or methacrolein being formed at least as the main product. As well as the desired
10 acrolein and acrylic acid product, the reaction of the alkane over heterogeneous catalysts with an oxygen-containing gas leads to a series of by-products: for example to the formation of CO₂ and CO.

It is known that the type of chemical composition of the mixed oxide (phase formation and formation of reaction
15 sites) and also the type of physical structure (for example porosity, surface size, form of the catalyst) and the type of heat removal can greatly influence the ability to form product (selectivity) and the productivity (space-time
20 yield). In the case of alkane oxidation, the catalyst used is generally mixed oxides which, in their chemical and physical makeup, have a complex structure.

STATE OF THE ART

The reaction of propane with oxygen or air over the known
25 Mo-V-Te catalysts leads generally to the formation of acrylic acid. Acrolein is formed only in traces, if at all. The publications for the preparation of acrylic acid are numerous and form the subject-matter of many scientific discussions.

30 WO 2004105938 relates to the preparation of acrylic acid from propane using catalysts of the general formula

$\text{Te}_a\text{Mo}_1\text{V}_b\text{Nb}_c\text{O}_x$ (I) or $\text{Sb}_a'\text{Mo}_1\text{V}_b\text{O}_y$ (I'); this forms acrolein with selectivities of 0 to 0.3%.

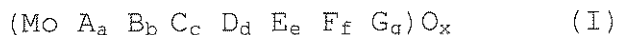
WO 2006058998 describes the preparation of a catalyst comprising tantalum of the general formula $\text{MoV}_a\text{XbTa}_c\text{Si}_d\text{O}_x$. The catalyst system is likewise used to prepare acrylic acid. Acrolein is formed with selectivities of less than 1% as a by-product.

From US 2005065370 is a process for preparing meth(acrylic acid) by the conversion of saturated hydrocarbons over a mixed oxide catalyst which comprises the elements Mo and V, and at least Te and Sb, and also one of the elements Nb, Ta, W, Ce and Ti, by virtue of the catalyst bed being interrupted by a further catalyst bed which consists of a mixed oxide catalyst comprising the elements Mo, Bi and Fe. In the examples, only statements about the acrylic acid selectivity are made.

Xiamen Daxue Xuebao, Ziran Kexueban (2004), 43(2), 203-207 describes the conversion of propane to acrolein over Mo-V-Te catalysts; in this case, propane conversions around 20% and acrolein selectivities of up to 30% are obtained. Cuihua Xuebao (2002), 23(3), 281-284 describes conversions of propane to acrolein over $\text{Ag}_{0.3}\text{MoP}_{0.6}\text{O}$ and $\text{Ce}_{0.1}\text{Ag}_{0.3}\text{MoP}_{0.6}\text{O}_y$.

According to US 2006004226, acrolein and acrylic acid are formed by converting propane over two reaction zones (catalysts). In the first stage, a mixture of propane and propene is formed; after the second stage, the condensate contains, inter alia, 98.48% by weight of acrylic acid and 0.002% by weight of acrolein.

In a first aspect, there is provided mixed oxide catalysts of the general formula



in which:

A: bismuth,

B: at least one of the elements comprising nickel and/or cobalt,

C: at least one of the elements comprising Fe, Ce, Mn, Cr, V,

D: at least one of the elements comprising W, P,

E: at least one of the elements comprising Li, K, Na, Rb, Cs, Mg, Ca, Ba, Sr,

F: at least one of the elements comprising Zn, Nb, Se, Te, Sm, Gd, La, Y, Pd, Pt, Ru, Ag, Au,

G: at least one of the elements comprising Si, Al, Ti, Zr

and

$$a = 0 - 1$$

$$b = 0 - 1$$

$$c = 0.001 - 1$$

$$d = 0.01 - 2$$

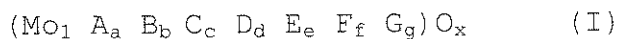
$$e = 0 - 1$$

$$f = 0.01 - 1.5$$

$$g = 0 - 800,$$

x = number which is determined by the valency and frequency of the elements other than oxygen.

In a second aspect, there is provided a process for preparing aldehydes, with or without acids, by catalytic oxidation of alkanes or mixtures of alkanes and the corresponding olefins with air or oxygen, optionally in the presence of inert gases, steam or offgases from the reaction at elevated temperatures, characterized in that a catalyst of the general formula



is used, in which:

A: bismuth,

B: at least one of the elements comprising nickel and/or cobalt,

C: at least one of the elements comprising Fe, Ce, Mn, Cr, V,

D: at least one of the elements comprising W, P,

E: at least one of the elements comprising Li, K, Na, Rb, Cs, Mg, Ca, Ba, Sr,

F: at least one of the elements comprising Zn, Nb, Se, Te, Sm, Gd, La, Y, Pd, Pt, Ru, Ag, Au,

G: at least one of the elements comprising Si, Al, Ti, Zr

and

$$a = 0 - 1$$

$$b = 0 - 1 \quad c = 0.001 - 1$$

$$d = 0.01 - 2$$

$$e = 0.001 - 1$$

$$f = 0.01 - 1.5$$

$$g = 0 - 800,$$

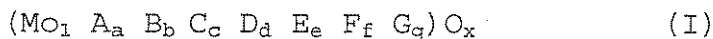
x = number which is determined by the valency and frequency of the elements other than oxygen.

Problem and scope

The present invention has for its object to provide a process for preparing aldehydes, in which especially acrolein or else mixtures of acrolein and acrylic acid are formed in good yields from propane or from propane/propene

mixtures by oxidation with oxygen. The oxidation is optionally performed in the presence of inert gases, steam or offgases at elevated temperatures and in the presence of a heterogeneous mixed oxide catalyst.

- 5 The alkane or the mixture of alkane and olefin is converted to the aldehyde and acid oxidation products at elevated temperature and a ratio between alkane, oxygen, inert gas(es) and water of generally 1:0.5-5:0-10:0-18. In a preferred embodiment, the water content is 0.
- 10 The inert gases which can be used are all gaseous compounds which behave inertly under the oxidation conditions described. For example, these may be nitrogen, helium or mixtures thereof. It is likewise possible to feed the "return gas" from the reactor back in.
- 15 The invention provides mixed oxide catalysts of the general formula



in which:

A: bismuth,

- 20 B: at least one of the elements comprising nickel and/or cobalt,

C: at least one of the elements comprising Fe, Ce, Mn, Cr, V,

D: at least one of the elements comprising W, P,

- 25 E: at least one of the elements comprising Li, K, Na, Rb, Cs, Mg, Ca, Ba, Sr,

F: at least one of the elements comprising Zn, Nb, Se, Te, Sm, Gd, La, Y, Pd, Pt, Ru, Ag, Au,

G: at least one of the elements comprising Si, Al, Ti, Zr

30 and

- a = 0 - 1, preferably 0-0.1,
b = 0 - 1, preferably 0-0.1,
c = 0.001 - 1, preferably 0.005-0.1,
d = 0.01 - 2, preferably 0.01-0.1,
5 e = 0 - 1, preferably 0-0.1,
f = 0.01 - 1.5, preferably 0.01-0.8,
g = 0 - 800,

x = number which is determined by the valency and frequency of the elements other than oxygen.

- 10 The letters a to x represent the atomic ratios of the corresponding elements in relation to Mo.

Catalysts of the general formula I are particularly suitable catalytically active solids, for example for the conversion of propane or mixtures of propane and propene to
15 acrolein and acrylic acid, and are provided by a process which likewise forms part of the subject-matter of the invention. Particularly advantageously, the reaction is performed in reactors which allow the catalyst to be used as a fixed bed or fluidized bed. However, it is likewise
20 possible to apply the catalyst to the wall of the reaction chamber. At this point, it should be noted that catalysts of the general formula I can also be utilized for the conversion of isobutane or mixtures of isobutane and isobutene to methacrolein and methacrylic acid.

- 25 In the processes known from the prior art, proceeding from suitable sources of the components of the multimetal oxide composition, a very intimate, preferably finely divided, dry mixture is obtained and is treated thermally at temperatures of > 150 to 700°C, preferably 400 to 700°C or
30 especially 450 to 600°C. The thermal treatment can in principle be effected either under an oxidizing atmosphere or under an inert atmosphere and optionally in the presence of steam. Useful oxidizing atmospheres include, for example, air, air enriched with molecular oxygen or air

depleted of oxygen. However, preference is given to performing the thermal treatment under inert atmosphere, i.e., for example, under molecular nitrogen and/or noble gas. Typically, the thermal treatment is effected at standard pressure (1 atm). It will be appreciated that the thermal treatment can also be effected under reduced pressure or under elevated pressure.

Overall, the thermal treatment may take from 0.25 h up to 24 h or more and be effected in several steps. Preference is given to 0.25 to 10 h.

Preference is given to effecting the thermal treatment of the dry mixture under inert atmosphere at a temperature of > 150 to 400°C or 250 to 450°C (= predecomposition step). Thereafter, the thermal treatment is appropriately continued under inert gas at temperatures of > 450 to 700°C, in particular 450 to 600°C.

Should a shaping be required, it is advantageous to interrupt the thermal treatment in the temperature range of 420 to 490°C, to perform the shaping and then to continue the thermal treatment in the temperature range of 490 to 700°C, especially up to 600°C. However, it is also possible to shape the finished calcined powder.

The starting compounds can be mixed intimately in dry or in wet form.

When the preparation is effected in wet form, the starting compounds are mixed with one another in the form of aqueous solutions and/or suspensions. Subsequently, the mixture is generally dried at 60°C to < 150°C, especially up to 130°C, and treated thermally after the drying.

Useful sources for the for the constituents of the mixed oxide catalyst of the formula (I) may, in the performance of the above-described preparation method, be all of those which are capable of forming oxides and/or hydroxides in

the course of heating (optionally under air). Of course, such starting compounds used may also partly or exclusively already be oxides and/or hydroxides of the elemental constituents.

- 5 The components are ideally dissolved in the form of their compounds selected from the group of ammonium compounds, oxalates, hydroxides, carbonates, phosphates, acetates, carbonyls and/or nitrates, individually or together, and mixed with one another. Particular preference is given to
10 carbonates, nitrates and phosphates or mixtures thereof. It is likewise possible to use acids of the salts, for example nitric acid, phosphoric acid or carbonic acid, or suspensions of the corresponding metal oxides.

- Depending on the type of metal salts which are used in the
15 precipitation, it may be necessary to add salts and acids or mixtures thereof to the precipitation mixture. Ideally, ammonia or ammonium salts are used here, for example ammonium carbonate, ammonium heptamolybdate or metal nitrates, for example cobalt nitrate; it is likewise
20 possible to use the corresponding acids, for example nitric acid in the amounts needed to establish the ionic ratio. The pH during the precipitation is typically < 8, especially < 7.

- Likewise of significance is the temperature of the
25 precipitation solution. It may thus be that the later activity of the catalyst is reduced significantly in the case of too high a temperature. The precipitation can in principle be performed at temperatures of 25 to 90°C.

- The coprecipitate can be precipitated in one stage.
30 Particular preference is given to performing the precipitation in several stages by stepwise addition of the individual components or mixtures thereof. The number of precipitation stages is not limited in principle. However, preference is given to 1 to 3 precipitation stages.

The resulting suspension can be processed further directly, or it is advantageously allowed to mature for > 0 to 24 hours. Preference is given to > 0 to 12 hours, particular preference to 0 to 6 hours. It is obvious that the
5 precipitation suspension is homogenized before the further processing, for example by stirring.

After the maturation, the liquid of the suspension can be removed by evaporation, centrifugation or filtration. It is likewise possible to evaporate the liquid and
10 simultaneously to dry the solid, which can be done, for example, by spray-drying. The liquid should be evaporated at a temperature of 80 to 130°C. The solid can be dried with air, oxygenous inert gases or inert gases, for example nitrogen. When the drying is performed in an oven, the
15 temperature should be between 100 and 150°C. In a spray dryer, the starting temperature of the drying medium should be 200 to 500°C, and a temperature on deposition of the dried powder of 80 to 200°C should be provided. The resulting particles should preferably have a particle size
20 distribution of 15 to 160 μm with a mean particle diameter between 15 and 80 μm .

The dried powder can in principle be calcined in a wide variety of different oven types, for example in a forced-air oven, rotary tube, tray oven, shaft oven or belt oven.
25 The control quality and the quality of temperature detection of the oven should be as high as possible. The residence time of the powder in the oven should, according to the oven type, be between 0.25 and 10 h.

It is likewise possible to perform the calcination and the
30 thermal decomposition of the salts which occurs at the same time in one or more stages. It is possible to utilize temperatures of 200 to 650°C, especially 300° to 650°. The thermal decomposition can be performed with addition of inert gas, composed of mixtures of oxygen with an inert
35 gas.

The inert gases usable are, for example, nitrogen, helium, steam or mixtures of these gases.

After the thermal treatment, the resulting catalyst material can appropriately be comminuted and optionally
5 classified.

The powder thus obtained is suitable as a catalyst. For industrial use, it is particularly appropriate, after addition of commercial shaping media and binders, to shape the powder. This can be done by tableting, extrusion or by
10 coating a support. In this context, the geometric shape of the support is not limiting. Instead, it is guided by the requirements of the reactor (for example tube diameter, length of the catalyst bed). For example, the support may be a pyramid, a cylinder, a saddle, a sphere, a ring or a
15 polygon, but it may also be a wall of the reactor in which the conversion of the reactants takes place.

Useful materials for the support bodies in accordance with the invention include especially aluminium oxide, titanium oxide, silicon dioxide, silicates such as clay, kaolin,
20 pumice, aluminium silicate and magnesium silicate, silicon carbide and zirconium oxide.

The surface of the support body may either be smooth or rough. Advantageously, the surface of the support body is rough.

25 The thickness of the active oxide composition coating present on the coated catalysts is typically 10 to 1000 μm . It may, though, also be 50 to 700 μ , 100 to 600 μ , or 150 to 400 μ . Possible coating thicknesses are also 10 to 500 μm , 100 to 400 μm or 150 to 300 μm .

30 The binders used may be various oils, polyols, for example glycerol and polyvinyl alcohols, celluloses, saccharides, acrylates and alkyl derivatives, mixtures or condensates thereof. In a shaping of the catalyst powder, the catalyst

should preferably be aftertreated thermally in the temperature range of 490 to 650°C, such that the active composition for use in industrial reactors solidifies.

The invention likewise provides a process for oxidation of
5 alkanes and mixtures of alkanes/olefins to prepare unsaturated aldehydes, with or without the corresponding acids, in the presence of the inventive catalysts.

The olefins differ by one double bond from the alkanes used in each case.

10 The inventive reaction to prepare acrolein or optionally mixtures of acrolein and acrylic acid is performed generally at temperatures of 350-500°C and a pressure of 1.0-2.2 bara. The reactants, alkane or a mixture of alkane and olefin, are converted to the oxidation products,
15 aldehyde, with or without acid, at relatively high temperatures and a ratio between alkane, oxygen, inert gas(es) and water of preferably 1:0.5-5:0-10:0-15, at a loading with 2-20 mol of alkane or of a mixture of alkane and olefin/l of catalyst bed/h.

20 Instead of inert gas, the offgas from the reaction, from which the condensable constituents have been removed, can be used. Particularly good results are obtained in the case of use of tube bundle reactors, plate reactors (for example EP 0 995 491; EP 1 147 807) or wall reactors (for example
25 Redlingshoefer H., Fischer A., et al., Ind. Eng. Chem. Res. 2003, 42, 5482-5488; EP 1 234 612), in which the catalyst has been applied to the wall.

The internal diameter of the reaction tubes or the distance between the plates should be 18 to 28 mm, preferably 20 to
30 26 mm; the wall thickness of the iron-containing steel should be between 1 and 3.5 mm. A typical reactor length is 3.00 to 4.00 m. The catalyst is preferably used homogeneously over the reactor length without dilution with

shaped diluent bodies; of course, the application may necessitate dilution, for example with shaped inert bodies.

The inventive catalysts, even at high specific loading, have an improved activity and selectivity for the
5 preparation of acrolein.

The invention will be explained with reference to working examples. Definitions used are:

the yield (%) of the product as
$$\frac{(\text{mol/h of product formed})}{(\text{mol/h of reactant supplied})} \times 100$$

10

the conversion of the alkane (%) as

$$[1 - (\text{mol/h of alkane leaving the reaction tube}) / (\text{mol/h of alkane entering the reaction tube})] \times 100$$

the selectivity (%) as
15 $(\text{yield of the product} / \text{conversion}) \times 100$

The invention detailed is, in order to improve understanding, described by the examples which follow, but is not restricted to these examples.

EXAMPLES

Example 1

A solution I was prepared by dissolving 2118.6 g of ammonium heptamolybdate in 2.7 l of water at 80°C. A
5 solution II was obtained at 80°C by dissolving the desired amount of $\text{H}_2\text{TeO}_4 \cdot 2 \text{H}_2\text{O}$ and cobalt nitrate. The two solutions were combined with stirring and the slurry (suspension) which formed was concentrated to dryness. The still moist powder obtained was dried at 150°C and
10 converted to the oxides at a temperature of 600°C. The mixed metal oxide powder obtained has the composition $(\text{MoCo}_{0.1}\text{Te}_{0.2})\text{O}_x$.

Example 2

The catalyst of Example 1 was contacted with a mixture of
15 the composition of one part of propane (chemical grade) (50% of the total amount of the mixture) and one part of oxygen (50% of the total amount of the mixture). The space velocity which arose was 3000 h^{-1} . The temperature of the heat carrier was 450°C. The conversion of the propane was
20 48.9 mol%; the product selectivity for acrolein was 32%.

Example 3

A solution I was prepared by dissolving 2118.6 g of ammonium heptamolybdate in 2.7 l of water at 80°C. A
25 solution II was obtained at 80°C by dissolving the desired amount of bismuth(III) nitrate and chromium(III) nitrate. The two solutions were combined with stirring and the slurry which formed was concentrated to dryness. The still moist powder obtained was dried at 150°C and converted to the oxides at a temperature of 600°C. The mixed metal oxide
30 powder obtained has the composition $(\text{MoCr}_{0.0286}\text{Bi}_{0.05})\text{O}_x$.

Example 4

The catalyst of Example 3 was contacted with a mixture of the composition of one part of propane (chemical grade) and one part of oxygen. The space velocity which arose was
5 3000 h⁻¹. The temperature of the heat carrier was 500°C. The conversion of the propane was 38 mol%; the product selectivity for acrolein was 43%.

Example 5

The product gas of Example 4 was recycled and converted
10 over the catalyst of Example 3. The space velocity which arose was 3000 h⁻¹. The temperature of the heat carrier was 500°C. The conversion of the propane was 76 mol%; the product yield of acrolein was 33%.

Example 6

15 A solution I was prepared by dissolving 2118.6 g of ammonium heptamolybdate in 2.7 l of water at 80°C. A solution II was obtained at 80°C by dissolving the desired amount of chromium(III) nitrate and H₂TeO₄ · 2 H₂O. The two solutions were combined with stirring and the slurry which
20 formed was concentrated to dryness. The still moist powder obtained was dried at 150°C and converted to the oxides at a temperature of 600°C. The mixed metal oxide powder obtained has the composition (MoCr_{0.0286}Te_{0.05})O_x.

Example 7

25 The catalyst of Example 6 was contacted with a mixture of the composition of one part of propane (chemical grade) and one part of oxygen. The space velocity which arose was 3000 h⁻¹. The temperature of the heat carrier was 450°C. The conversion of the propane was 27.5 mol%; the product
30 selectivity for acrolein was 58%.

Example 8

A solution I was prepared by dissolving 2118.6 g of ammonium heptamolybdate in 2.7 l of water at 80°C. A solution II was obtained at 80°C by dissolving the desired amount of chromium(III) nitrate, H_3PO_4 and $\text{H}_2\text{TeO}_4 \cdot 2 \text{H}_2\text{O}$. The two solutions were combined with stirring and the slurry which formed was concentrated to dryness. The still moist powder obtained was dried at 150°C and converted to the oxides at a temperature of 600°C. The mixed metal oxide powder obtained has the composition $(\text{MoCr}_{0.0286}\text{Te}_{0.05}\text{P}_{0.05})\text{O}_x$.

Example 9

The catalyst of Example 8 was contacted with a mixture of the composition of one part of propane (chemical grade) and one part of oxygen. The space velocity which arose was 3000 h^{-1} . The temperature of the heat carrier was 450°C. The conversion of the propane was 30 mol%; the product selectivity for acrolein was 70%.

Example 10

A solution I was prepared by dissolving 2118.6 g of ammonium heptamolybdate in 2.7 l of water at 80°C. A solution II was obtained at 80°C by dissolving the desired amount of chromium(III) nitrate, cobalt(II) nitrate and $\text{H}_2\text{TeO}_4 \cdot 2 \text{H}_2\text{O}$. The two solutions were concentrated with stirring and the slurry which formed was concentrated to dryness. The still moist powder obtained was dried at 150°C and converted to the oxides at a temperature of 600°C. The mixed metal oxide powder obtained has the composition $(\text{MoCr}_{0.0286}\text{Te}_{0.05}\text{Co}_{0.15})\text{O}_x$.

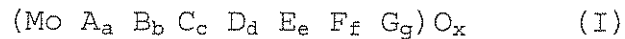
Example 11

The catalyst of the composition $(\text{MoCr}_{0.0286}\text{Te}_{0.05}\text{Co}_{0.8})\text{O}_x$ was contacted with a mixture of the composition of 1.2 parts of propane (chemical grade) and one part of oxygen. The space

velocity which arose was 3000 h^{-1} . The temperature of the heat carrier was 450°C . The conversion of the propane was 18 mol%; the product selectivity for acrolein was 72%.

Claims

1. Mixed oxide catalysts of the general formula



in which:

5 A: bismuth,

B: at least one of the elements comprising nickel and/or cobalt,

C: at least one of the elements comprising Fe, Ce, Mn, Cr, V,

10 D: at least one of the elements comprising W, P,

E: at least one of the elements comprising Li, K, Na, Rb, Cs, Mg, Ca, Ba, Sr,

F: at least one of the elements comprising Zn, Nb, Se, Te, Sm, Gd, La, Y, Pd, Pt, Ru, Ag, Au,

15 G: at least one of the elements comprising Si, Al, Ti, Zr

and

a = 0 - 1

b = 0 - 1

c = 0.001 - 1

20 d = 0.01 - 2

e = 0 - 1

f = 0.01 - 1.5

g = 0 - 800,

25 x = number which is determined by the valency and frequency of the elements other than oxygen.

2. Mixed oxide catalysts according to Claim 1, characterized in that the pulverulent mixed oxide catalyst has been applied to inert support materials or is extruded as a bulk material.

3. Process for preparing mixed oxide catalysts of claim 1, characterized in that solutions of compounds of the metals present in the mixed oxide catalysts of claim 1 are mixed, coprecipitates are prepared, and the resulting pulverulent solid is isolated, dried, treated thermally and optionally shaped.
4. Process according to Claim 3, characterized in that the pH during the preparation of the coprecipitate(s) is < 8 .
5. Process according to Claims 3 and 4, characterized in that compounds of the metals present in the catalyst of the formula (I) selected from the group consisting of ammonium or amine compounds, oxalates, carbonates, phosphates, acetates, carbonyls, hydroxides, oxides or nitrates, individually or together, are used.
6. Process according to Claims 3 to 5, characterized in that carbonates, hydroxides, oxides, nitrates or phosphates or mixtures of these salts are used.
7. Process according to Claims 3 to 6, characterized in that the anions of the acids corresponding to the salts used are used if appropriate.
8. Process according to Claims 3 to 7, characterized in that ammonium carbonate, ammonium heptamolybdate and at least one metal nitrate including chromium(III) nitrate, bismuth nitrate, cobalt nitrate; and/or if appropriate nitric acid are used to prepare the coprecipitate.
9. Process according to Claims 3 to 8, characterized in that the precipitation is performed at temperatures of 5 to 90°C .

10. Process according to Claim 9, characterized in that the precipitation is performed at temperatures of 20 to 90°C.
- 5 11. Process according to Claims 3 to 10, characterized in that the suspension obtained by precipitation is matured for ≥ 0 to 24 hours, preferably ≥ 0 to 12 hours, more preferably ≥ 0 to 6 hours.
12. Process according to Claims 3 to 11, characterized in that the coprecipitate is removed and dried.
- 10 13. Process according to Claims 3 to 12, characterized in that the dried coprecipitate, before the calcination, consists of spray-dried particles having a particle size distribution of 15 to 160 μm .
- 15 14. Process according to Claim 13, characterized in that the mean particle size distribution of the dried coprecipitate is between 15 μm and 80 μm .
- 20 15. Process according to Claims 3-14, characterized in that the residence time of the dried powder in the oven for thermal treatment is between 0.25 and 13 h, in the course of which temperatures of > 150 to 700°C are established.
16. Process according to Claims 3 to 15, characterized in that the thermal treatment is performed in one or more stages.
- 25 17. Process according to Claims 15 and 16, characterized in that the thermal treatment is performed in an atmosphere composed of inert gas, composed of mixtures of oxygen with an inert gas and/or in the presence or absence of steam.

18. Process according to Claims 15 to 17, characterized in that the thermally treated powder is shaped by tableting, extrusion, or applied to a support.
19. Process according to Claims 3 and 18, characterized in that, after the catalyst powder has been shaped, the shaped body thus obtained is heat-treated within a temperature range of 450 to 650°C.
20. Process for preparing aldehydes, with or without acids, by catalytic oxidation of alkanes or mixtures of alkanes and the corresponding olefins with air or oxygen, optionally in the presence of inert gases, steam or offgases from the reaction at elevated temperatures, characterized in that a catalyst of the general formula
- $$(Mo_1 A_a B_b C_c D_d E_e F_f G_g)O_x \quad (I)$$
- is used, in which:
- A: bismuth,
- B: at least one of the elements comprising nickel and/or cobalt,
- C: at least one of the elements comprising Fe, Ce, Mn, Cr, V,
- D: at least one of the elements comprising W, P,
- E: at least one of the elements comprising Li, K, Na, Rb, Cs, Mg, Ca, Ba, Sr,
- F: at least one of the elements comprising Zn, Nb, Se, Te, Sm, Gd, La, Y, Pd, Pt, Ru, Ag, Au,
- G: at least one of the elements comprising Si, Al, Ti, Zr
- and
- a = 0 - 1
- b = 0 - 1

c = 0.001 - 1

d = 0.01 - 2

e = 0.001 - 1

f = 0.01 - 1.5

5 g = 0 - 800,

x = number which is determined by the valency and frequency of the elements other than oxygen.

10 21. Process according to Claim 20, characterized in that acrolein or acrolein and acrylic acid is prepared by oxidizing propane or propene.

22. Process according to Claim 20, characterized in that methacrolein or methacrolein and methacrylic acid is prepared by oxidizing isobutane or isobutene.

15 23. Process according to Claims 20 to 22, characterized in that the catalyst is contacted with a reaction gas mixture which comprises alkane or a mixture of alkane and the corresponding olefin, oxygen and inert gas and water in a ratio of 1:0.5-5:0-10:0-18.