IN THE MATTER OF a Singapore Application corresponding to PCT Application PCT/FR95/00407

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(54) Title: COATED CATALYTIC COMPOSITIONS INCLUDING NICKEL, COBALT AND MOLYBDENUM, AND USE THEREOF FOR PREPARING UNSATURATED ALDEHYDES

(54) Titre: COMPOSITIONS CATALYTIQUES DU TYPE ENROBEES, COMPRENANT DU NICKEL, COBALT, MOLYBDENE ET LEUR UTILISATION POUR LA PREPARATION D'ALDEHYDES INSATURES

(57) Abstract

Catalytic compositions including a carrier coated with an active phase based, in particular, on bismuth, molybdenum and/or tungsten, cobalt, nickel, iron and oxygen, and doped with phosphorus and at least one alkaline element, said active phase constituting 15-33 wt % of the catalytic composition, wherein the active phase has an atomic ratio 100 x (P + alkaline elements)/Ni of 0.9-10. The use of such catalytic compositions for preparing unsaturated aldehydes by oxidising the corresponding olefins is also disclosed.

(57) Abrégé

La présente invention a trait à des compositions catalytiques comprenant un support enrobé d'une phase active à base notamment de bismuth, de molybdène et/ou de tungstène, de cobalt, de nickel, de fer, d'oxygène, dopée par du phosphore et au moins un élément alcalin, ladite phase active représentant 15 à 33 % en poids de la composition catalytique, caractérisée en ce que la phase active présente un rapport atomique 100 x (P + éléments alcalins) / Ni compris entre 0,9 et 10. L'invention concerne de même l'utilisation de telles compositions catalytiques pour l'obtention d'aldéhydes insaturés par oxydation des oléfines correspondantes.

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CATALYTIC COMPOSITIONS OF THE COATED TYPE COMPRISING NICKEL, COBALT AND MOLYBDENUM AND THEIR USE FOR THE PREPARATION OF UNSATURATED ALDEHYDES

The present invention relates to catalysts comprising a support on which an active phase is deposited which is based, in particular, on molybdenum, nickel, cobalt, bismuth and iron and is doped with phosphorus and at least one alkali metal element.

The invention likewise relates to the use of such catalytic compositions for the preparation of unsaturated aldehydes by oxidation of the corresponding olefins.

The use of catalytic compositions based in particular on molybdenum, bismuth and iron to prepare aldehydes by oxidation of an olefin is well known to the person skilled in the art and has been the subject of much research.

Various types of catalysts are thus employed to carry out this reaction. The first category consists of catalytic compositions which are in a mass form, alone or mixed with an inert diluent (support). These compositions may, inter alia, be in the form of granules, extrudates or pellets.

Although such catalysts are productive, they have the disadvantage of being difficult to employ in a fixed bed on an industrial scale. In effect, under these conditions, it is possible to observe a local increase in temperature in the catalyst bed, which may

be the origin of reactor runaway.

This is one of the reasons for development of catalysts comprising an inert support on which a catalytic active phase is deposited. This facilitates the control of the temperature within the fixed catalyst bed, and more precisely the uniformity of this temperature.

Nevertheless, this particular embodiment of the catalyst implies that an important part of the said catalyst is constituted by the support. In effect, the latter commonly represents more than half of the weight of the finished catalyst. Thus the quantity of active phase in the composition of the coated catalysts is considerably reduced relative to that which is present in the diluted mass catalysts. A direct consequence of this is to lower greatly the productivity of the coated catalysts.

A number of solutions may be considered for making such catalysts more attractive.

The first would consist in increasing either the size of the industrial installation or the reaction temperature, so as to retain the production capacity which would be achieved using a mass catalyst. However, these measures give rise not only to economic problems but also to problems linked directly to the chemistry of the reaction and to the performance of the catalyst. In fact, with an increase in temperature, the selectivity for aldehyde produced is decreased and the

catalyst used under these conditions becomes inactive more rapidly than a catalyst employed at lower temperatures.

Another solution would be to increase the proportion of the active phase of the final catalyst, that is to increase the thickness of the layer deposited on the support. However, in such a case the mechanical strength of the resulting catalyst, and more particularly its attrition resistance, would be inadequate for application on an industrial scale in a fixed bed.

Another possible solution, and certainly the most satisfactory, would be to add to the active phase dopants which are capable of increasing the selectivity for aldehyde produced of the catalyst. Proposals have therefore been made to add additives such as phosphorus and potassium to the catalytic composition. The use of such additives has proved to be relatively complex. In effect, although these compounds have a definite role with regard to the selectivity of the reaction for aldehyde, they cause a drop in catalyst performance in terms of activity if the proportion of these constituents in the active phase is too great.

The present invention relates to a catalyst composition of the coated type which does not have the abovementioned disadvantages. Thus the said composition, when employed in oxidation reactions for the preparation of unsaturated aldehydes, makes it

possible to obtain results which are improved in terms of selectivity - and consequently of yield of aldehyde produced, while retaining a productivity which is higher than that of the conventional coated catalysts having the same content of dopants.

Moreover, a certain advantage lies in the observation that the performance of the composition according to the invention is of great stability over time, and therefore its useful life is considerably increased.

Thus the invention relates to a catalytic composition comprising a support coated with an active phase which is based on bismuth, molybdenum and/or tungsten, cobalt, nickel, iron and oxygen and is doped with phosphorus and at least one alkali metal element, the said active phase representing from 15 to 33 % by weight of the catalytic composition. In addition, the active phase in the composition according to the invention has an atomic ratio 100 x (P + alkali metal elements)/Ni of between 0.9 and 10.

The invention relates secondly to a process for the preparation of α-β-unsaturated aldehydes by oxidation of olefins in the gas phase in the presence of the catalytic composition mentioned above.

However, other advantages and characteristics of the invention will become clearer on reading the description and examples which follow.

As indicated earlier, the catalytic

composition according to the invention comprises a support on which an active phase is deposited.

The material making up the support is chosen such that it is inert under the conditions in which the catalytic composition is used. Examples of materials which may be employed in this context are silica, alumina, silica-alumina, sintered clay, diatomaceous earth, magnesium oxide, magnesium silicate and ceramic materials such as, for example, cordierite, mullite, porcelain, silicon nitride and silicon carbide.

More particularly, the support is in the form of beads with a diameter of between 0.5 and 6 mm.

The active phase which is a constituent element of the composition according to the invention is based on bismuth, molybdenum and/or tungsten, cobalt, nickel, iron and oxygen doped with phosphorus and at least one alkali metal element. More particularly, the alkali metal element is potassium.

In addition to the abovementioned constituent elements, the active phase may comprise other elements. Thus it is possible to include arsenic, boron or a mixture thereof. It is likewise possible to substitute part of the nickel/cobalt mixture - but while retaining these two elements in the composition - by manganese, magnesium, lead or a mixture thereof.

However, according to a preferred embodiment of the invention, the active phase is based on the elements cited in the first list.

The active phase in the catalytic composition according to the invention is additionally characterized by the atomic ratio 100 x (P + alkali metal elements)/Ni (referred to hereafter as atomic ratio). Thus, the active phase has an atomic ratio of between 0.9 and 10.

According to a particular embodiment of the invention, the atomic ratio is between 0.9 and 7.

The catalytic compositions according to the invention possess, moreover, an active phase in which the quantity of nickel, relative to nickel and cobalt together, is between 10 and 60 mol%.

It has been found quite surprisingly that the catalytic composition containing nickel, as defined earlier, may contain a much higher quantity of doping elements (the phosphorus and the alkali metal elements) than nickel-free compositions without, moreover, any disadvantageous effect being observed on the activity of the resulting catalytic compositions.

Consequently the compositions according to the invention, when employed in reactions for oxidation of olefins, are particularly selective for aldehyde and exhibit an acceptable productivity.

According to a particular embodiment, the atomic ratio of the alkali metal element to the phosphorus is from 0.3 to 3 inclusive.

This ratio is preferably from 0.5 to 2 inclusive.

As indicated beforehand, the catalytic composition comprises an active phase which is deposited on a support. The quantity of active phase represents from 15 to 33 % by weight of the catalytic composition. It preferably represents from 20 to 30 % by weight of the catalytic composition.

The active phase may be obtained by any conventional means.

It is possible, for example, to consider preparing the said active phase by mixing the oxides of the elements which constitute the active phase, or compounds which are capable of becoming oxides when heated to high temperatures. The mixture is then subjected to a calcination step which is, if desired, followed and/or preceded by the grinding of the said mixture (technique of forming a grog).

Another suitable method for the preparation of the active phase consists in preparing a mixture based on the constituent elements of the active phase, in carrying out a drying operation and then in calcining the resulting product.

The constituent elements which are employed according to this method may be used, in particular, in the form of oxides or of oxide precursors, such as the salts of inorganic or organic acids. Nitrates, sulphates, halides, ammonium salts, formate, oxalate, tartrate and acetate may be mentioned by way of example. Also suitable are oxide derivatives such as,

in particular, hydroxides, oxyhalides, alkoxides and glycoxides.

The said salts are then suspended or dissolved in any appropriate dispersion medium or solvent, preferably water.

The drying operation which is performed more particularly under a nonreducing atmosphere may be carried out by evaporation to dryness or by atomization.

According to the first variant, the drying is carried out in two stages: the first stage consists in evaporating the solvent or dispersion medium from the mixture, to dryness, the second in drying the paste thus obtained. In general the first stage is carried out with stirring at a temperature of from 20 to 100°C for the period which is required to obtain a nonflowing paste. The resulting paste is dried in a second stage under a preferably nonreducing atmosphere such as, for example, oxygen or air. The latter operation is carried out for an average period of 15 hours at a drying temperature of approximately 120°C.

According to the second variant, the drying is carried out by atomizing the solution or suspension by any means known to the person skilled in the art, for example "flash" atomizers such as those claimed in the French Patent Applications published under the following numbers: 2 257 326, 2 419 754 and 2 431 321, or else those of the BUCHI type. The temperature of

atomization is generally of the order of from 150 to 300°C and the atmosphere under which it is carried out is preferably nonreducing as indicated above.

The dried product is subsequently subjected to a calcination step under a nonreducing atmosphere at a temperature which is appropriate for the formation of oxides. This temperature is commonly between 200 and 1200°C.

Prior to the calcination step, the dried product may undergo a grinding step. It should be noted that the calcined product may if desired also undergo such treatment.

A third method which is suitable for the preparation of the active phase consists in carrying out one or more successive steps of precipitating the constituent elements which are present in soluble form. This step is carried out prior to drying, while retaining the other steps mentioned in the preceding variant.

The compounds which can be used as precipitating agent are chosen from those which combine with one or more of the constituent elements in the form of a compound which is insoluble in the medium, the said insoluble compound being an oxide precursor. Conventionally, but with no limitation, aqueous ammonia, hydrochloric acid and citric acid are suitable.

The precipitation is commonly carried out

with stirring.

The temperature at which it is carried out generally ranges between 20°C and the boiling temperature of the chosen solvent.

Finally, the precipitation step or steps may if necessary be followed by ageing steps. The latter consist in leaving the precipitate in suspension, with stirring, for a period ranging from approximately 30 minutes to 4 hours.

According to a preferred embodiment of the process for the preparation of the catalytic composition according to the invention an active phase is first of all prepared which is free of dopants, that is free of phosphorus and alkali metal elements; the latter are not introduced until the moment when the active phase is deposited on the support (coating).

Coating is the operation by which the beads of the support are gradually surrounded by an outer layer of active phase.

This operation is carried out in a manner known per se by the introduction of the said beads into a rotary coating apparatus. The latter is equipped with means for introducing particles of active phase whose size is preferably less tha 400 μm and with means for introducing an aqueous solution of adhesion agent. As mentioned earlier, and in accordance with an advantageous characteristic of the present process, the introduction of the dopants is therefore carried out

during this step.

More particularly, at least one compound of an alkali metal element, preferably potassium, and at least one phosphorus compound in the form of a solution, more particularly an aqueous solution, are introduced into the coating apparatus simultaneously with the catalytic composition which is free of the said dopants and a solution of an adhesion agent. The solubility in water of the phosphorus compound(s) and of the alkali metal element compound(s), measured at 25°C, is preferably greater than 10 g/l.

The said compounds are chosen from those which do not interfere with or are inert to the other components of the coating solution, in particular the adhesion agent and, if appropriate, other additives such as, for example, a pore-forming agent. These compounds may in addition be able to undergo decomposition by heat during the subsequent calcination.

In practice the addition of the chosen compounds of phosphorus and of the alkali metal element, especially of potassium, must impart to the aqueous solution a pH of between 3 and 11.

According to a first variant, compounds are employed which comprise one or other of the abovementioned dopants. Thus, compounds which may be mentioned as introducing the alkali metal element are potassium hydroxide and sodium hydroxide. As far as the

phosphorus-based compounds are concerned, it is possible to mention - with no limitation being intended - inorganic or organic phosphates or phosphoric acid.

According to a second, preferred, variant of the present invention at least one compound is used which is based on two types of dopants such as, for example, the dihydrogen phosphate of potassium or sodium or the monohydrogen phosphate of potassium or sodium.

It should be noted that it is entirely possible to consider combining the two preceding variants. This is particularly appropriate when, in employing the second variant, it is necessary to supplement one and/or other of the dopants.

According to a particular embodiment the compounds of phosphorus and of the alkali metal element are introduced into the aqueous solution of adhesion agent.

The coating operation is carried out in a rotary coating apparatus rotating at between 10 and 20 revolutions per minute, into which the quantity of beads of support required to cover the active phase is placed, these beads being in a rough and dedusted state. Then, via a chute, the ground intermediate catalytic composition and the aqueous solution of adhesion agent and of the compound(s) of phosphorus and of alkali metal element are introduced simultaneously.

In a preferred variant, the beads have been

wetted beforehand with an aqueous solution of adhesion agent which does not contain dopant.

The operation is continued until all of the coating solution and then all of the active phase have been used. Rotation is continued for several minutes to make sure that the layer of active phase on the beads is well settled.

The beads are then dried in hot air at between 80 and 150°C for from 10 to 30 minutes and are calcined.

According to a particular embodiment the calcination step is carried out in two stages. The first stage consists in raising the temperature over from 3 to 15 hours to between 450 and 500°C. In the second stage the mixture is cooled over from 3 to 10 hours.

In a preferred variant a second calcination is carried out in succession to, and under the same conditions of temperature variation as, the first calcination.

In another preferred variant the calcination temperature is 480°C.

The present invention relates finally to a process for the preparation of α-β-unsaturated aldehydes by oxidation in the gas phase of the corresponding olefins, the reaction being carried out in the presence of the catalytic composition according to the invention.

The invention is suitable more particularly for the preparation of acrolein or methacrolein by oxidation of propylene or isobutylene, respectively.

The reaction consists in introducing the olefin, an oxygen source and, if desired, water into a reactor.

Oxygen, in pure form or diluted in inert gases such as nitrogen, oxides of carbon and/or noble gases may be used as oxygen source. It should be noted that such gases may originate from the recycling of the gases in the process.

The oxygen source employed is advantageously air.

The quantity of olefin in the feed stream is commonly between 6 and 10 mol%.

The quantity of oxygen present in the feed stream is generally between 10 and 15 mol%.

The quantity of water vapour introduced is commonly between 0 and 40 mol%. The quantity of water is preferably between 20 and 40 mol%.

The abovementioned inert gases represent the remaining amount to 100 %.

In general the reaction temperature is approximately from 100 to 450°C.

The pressure of the reactants on entering the reactor is between 1 and 5 bar. The pressure is more particularly between 1 and 3 bar.

The pressure is preferably slightly greater

than atmospheric pressure, in order to take account of the pressure losses within the apparatus.

As a general rule the present reaction is carried out in the presence of a fixed catalyst bed, although the use of fluidized beds may be considered.

Specific but nonlimiting examples of the invention will now be presented.

EXAMPLE 1

Preparation of a catalyst of general formula

$Co_{6.1}Ni_{3.8}Fe_1Bi_1Mo_{12}P_{0.05}K_{0.1}O_\alpha$

1- Preparation of the dopant-free active phase.

The following solutions are prepared:

A: 167.6 g of ammonium heptamolybdate $[(NH_4)_6Mo_7O_{24}\cdot 4H_2O]$

760 ml of demineralized water

The components are mixed at 80°C with stirring.

B: (a) 32.1 g of iron nitrate $[Fe(NO_3)_3\cdot 9H_2O]$

25 ml of demineralized water

(b) 38.4 g of bismuth nitrate $[Bi(NO_3)_3\cdot 5H_2O]$

4 ml of pure nitric acid (d = 1.33) which is then diluted with 28.5 ml of water added dropwise with stirring

Solution (a) is added dropwise to solution (b).

C: (a) 138 g of cobalt nitrate $[Co(No_3)_2\cdot 6H_2O]$

90 ml of water

(b) 91.9 g of nickel nitrate $[Ni(No_3)_2\cdot 6H_2O]$

10 ml of water

Solutions (a) and (b) are then mixed.

Solution B is slowly added with stirring to solution C.

The resulting mixture is introduced over 30 minutes into solution A with vigorous stirring. The pH of the medium is 2.05 at the end of addition, and a pink suspension is obtained.

150 ml of aqueous ammonia (d = 0.92) are added to the suspension over 20 minutes with stirring. The pH at the end of the introduction is 7.1, and a beige-brown suspension is obtained.

The suspension is then heated at 60°C for 4 hours with stirring.

The medium is then left for 2 hours with neither heating nor stirring.

The solid is filtered off and washed using a total quantity of demineralized water of 1 litre.

The solid is then dried for 16 hours in the oven at 120°C and then calcined for 6 hours at 400°C in air and ground.

2 - <u>Preparation of the coated catalytic composition</u>.

Coating is carried out in a coating apparatus with a diameter of 20 cm which contains 100 g of clay beads sintered at 1100°C which have a surface roughness of 0.3 and a diameter of 4.8 mm. The beads are wetted beforehand with a first solution of glucose at a concentration of 0.1 g/l which is sprayed at a rate of

2.5 to 3.5 ml/min.

When all of the beads are wetted, a chute is used to introduce 44 g of dopant-free active phase over about 30 minutes. During the introduction of the powder, the coating apparatus continues to rotate, and 10 ml of a second solution of glucose at a concentration of 0.1 g/l, containing 13.56 g/l of K_2HPO_4 is sprayed onto the beads.

Once the solution and the dopant-free active phase together have been introduced, rotation is continued for several minutes approximately. The composition is then dried in a stream of hot air for 15 minutes.

The beads coated and dried in this way are introduced into ventilated ovens for calcination.

The temperature programme is as follows:

- increase to 240°C over 6 hours, then to 480°C over 8 hours;
- plateau of 6 hours at 480°C;
- cooling to 150°C over 10 hours;
- increase to 480°C over 10 hours;
- plateau of 6 hours at 480°C;
- final cooling to room temperature over 10 hours.

143. 5 g of the final catalyst are thus removed from the oven, the proportion by mass of active phase being 30 %.

EXAMPLE 2

Preparation of a catalyst of general formula

$Co_{6.1}Ni_{3.8}Fe_1Bi_1Mo_{12}P_{0.075}K_{0.15}O_\alpha$

1 - Preparation of the dopant-free active phase.

The procedure of Example 1 is repeated.

2 - Preparation of the coated catalytic composition.

The procedure of the preceding example is repeated except that the second solution of glucose (10 ml) contains 20.32 g/l of K_2HPO_4.

EXAMPLE 3, Comparative

Preparation of a catalyst of general formula:

$Co_{9.6}Fe_1Bi_1Mo_{12}P_{0.0125}K_{0.025}O_\alpha$

1 - Preparation of the dopant-free active phase.

The procedure of Example 1 is repeated except that no nickel nitrate (solution C) is added and that 230.2 g of cobalt nitrate are used instead.

2 - Preparation of the catalytic composition.

The procedure of Example 1 is repeated but the second solution of glucose contains 3.42 g/l of K_2HPO_4.

EXAMPLE 4

Preparation of a catalyst of general formula

$Co_9Ni_1Fe_1Bi_1Mo_{12}O_\alpha$

1 - Preparation of the dopant-free active phase.

The procedure of Example 1 is repeated except that solution C is obtained by mixing a solution comprising 207.5 g of cobalt nitrate in 90 ml of water

and a solution comprising 23 g of nickel nitrate in 10 ml of water.

2 - Preparation of the catalytic composition.

The procedure of Example 1 is repeated but the second solution of glucose contains no dopant.

Moreover, the procedure is carried out such that the resulting catalyst comprises 18 % by weight of active phase.

EXAMPLE 5

Preparation of a catalyst of general formula $Co_{6.1}Ni_{3.8}Fe_1Bi_1Mo_{12}O_\alpha$

1 - Preparation of the dopant-free active phase.

The procedure of Example 1 is repeated.

2 - Preparation of the catalytic composition.

The procedure of Example 1 is repeated but the second solution of glucose contains no dopant.

Moreover, the procedure is carried out such that the resulting catalyst comprises 18 % by weight of active phase.

EXAMPLE 6, Comparative

Preparation of a catalyst of general formula: $Co_{9.6}Fe_1Bi_1Mo_{12}O_\alpha$

1 - Preparation of the dopant-free active phase.

The procedure of Example 1 is repeated except that solution C comprises 230.2 g of cobalt nitrate in 90 ml of water.

2 - Preparation of the catalytic composition.

The procedure of Example 1 is repeated but

the second solution of glucose contains no dopant.

Moreover, the procedure is carried out such that the resulting catalyst comprises 18 % by weight of active phase.

EXAMPLE 7

The catalyst performance data described in Examples 1, 2 and 3 (comparative) were determined under the following conditions:

90 ml of coated, undiluted catalyst are present in a reactor which is 80 cm high and has an internal diameter of 15.5 mm.

The gases entering the reactor consist of a mixture of propylene, air and water in the following molar proportions (expressed in %): 7/57/36.

The pressure in the reactor is maintained at 1.8 bar absolute.

The hourly space velocity, defined by the ratio of total gas flow rate (standard l/h) to the volume of catalyst, is 1265 h^{-1}, corresponding to a propylene charge of 166 g per hour per litre of catalyst.

The degree of conversion of the propylene, X_{C3H6}, is defined by the following ratio:

$$\frac{\text{moles of converted propylene}}{\text{moles of propylene introduced}} \times 100$$

The selectivity for product i, Si, is defined as the following ratio:

$$\frac{\text{moles of product i formed}}{\text{moles of propylene converted}} \times 100$$

The yield of product i, Ri, is defined as the product of X_{C3H6} and Si.

The catalytic performance of the catalysts is measured after 30 hours in the presence of the reactants.

TABLE 1

EXAMPLE	T_{bath} (°C)	X_{C3H6} (%)	S_{acro} (%)	S_{acry} (%)	S_{COx} (%)	R_{acro} (%)
Example 1	330	89.5	87.7	7.2	1.9	78.5
Example 2	330	82.7	90.9	4.5	1.5	75.2
Example 3 comparative	330	94.5	78.0	11.0	5.2	73.7

acro = acrolein

acry = acrylic acid

COx = combustion products

EXAMPLE 8

Test of stability over time.

The stability of the performance of the catalysts described in Example 2 and Example 3 (comparative) was determined under the following conditions:

2 litres of coated, undiluted catalyst are present in a reactor with an internal diameter of 26 mm which is 4 metres high.

The gases entering the reactor consist of a mixture of propylene, air and water in molar proportions (expressed in %): 8.9/62.5/28.6.

The pressure in the reactor is maintained at 1.8 bar absolute.

The hourly space velocity, defined as in Example 3, is 1370 h^{-1}, corresponding to a propylene charge of 230 g per hour per litre of catalyst.

The tests are carried out while maintaining the propylene conversion at a constant value of approximately 90% while progressively increasing the bath temperature.

Table 2 makes it possible to compare the levels of bath temperature which are required to maintain constancy of conversion and of the catalytic performances of the catalysts of Example 2 and of Example 3 (comparative) during tests lasting approximately 2000 hours.

The degrees of conversion of the propylene,

X_{C3H6}, the selectivities Si and the yield Ri of the various products i are defined as in the preceding example.

TABLE 2

EXAMPLE	Catalyst formula	time (hours)	T_{bath} (°C)	X_{C3H6} (%)	S_{acro} (%)	R_{acro} (%)
Example 2	$Co_{6.1}$ $Ni_{3.8}$ Fe_1 Bi_1 Mo_{12} $P_{0.075}$ $K_{0.15}$ O_α	800	328	89.0	92.2	82.1
		1400	327	90.0	92.2	83
		1600	328	90.2	91.9	82.9
		1800	327.5	90.8	92.5	84.0
Example 3, comparative	$Co_{9.6}$ Fe_1 Bi_1 Mo_{12} $P_{0.0125}$ $K_{0.025}$ O_α	1400	343.5	89.5	86.0	77.0
		1600	345.5	89.9	85.2	76.6
		1800	347	91.3	84.0	76.7
		2000	352	90.7	83.0	75.3

This table clearly indicates that the catalysts according to the invention have a very considerably greater stability than those of the prior art, since after 1800 hours the bath temperature is identical to the initial temperature.

In contrast, it has increased by almost 10°C in the case of the prior art catalysts.

EXAMPLE 9

Accelerated ageing test

The dopant-free catalysts obtained in Examples 4, 5 and 6 (comparative) were tested under the following conditions:

A bed of 90 ml of coated catalyst diluted to a quarter of its volume with beads of noncoated clay is present in the reactor defined in Example 7.

The gases entering the reactor consist of a mixture of propylene, air and water in the following molar proportions (expressed in %): 7/57/36.

The pressure in the reactor is maintained at 1.8 bar absolute.

The hourly space velocity is 4285 h^{-1}, corresponding to a propylene charge of 562 g/h/l of active catalyst.

The ageing test is carried out by increasing the bath temperature over time (between 400 and 420°C).

The results of this catalytic test are collated in Table 3 below, which indicates the number of conversion points (X g) lost over 100 hours testing.

EXAMPLE	Catalyst formula	Δconversion
Example 4	$Co_9\ Ni_1\ Fe_1\ Bi_1\ Mo_{12}\ O_\alpha$	8
Example 5	$Co_{6.1}\ Ni_{3.8}\ Fe_1\ Bi_1\ Mo_{12}\ O_\alpha$	4
Example 6, Comparative	$Co_{9.6}\ Fe_1\ Bi_1\ Mo_{12}\ O_\alpha$	12

This table shows that the catalysts comprising nickel have a catalytic activity which is more stable over time than catalysts not containing nickel, and it is apparent, moreover, that this effect becomes more marked as the content of nickel in the active phase increases.

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CLAIMS

1. Catalytic composition comprising a support coated with an active phase which is based on bismuth, molybdenum and/or tungsten, cobalt, nickel, iron, oxygen and is doped with phosphorus and at least one alkali metal element, characterized in that the said active phase representing from 15 to 33 % by weight of the catalytic composition, and the active phase has an atomic ratio 100 x (P + alkali metal elements)/Ni of between 0.9 and 10.

2. Composition according to the preceding claim, characterized in that the atomic ratio is between 0.9 and 7.

3. Catalytic composition according to any one of the preceding claims, characterized in that the atomic ratio of the alkali metal element to the phosphorus is from 0.3 to 3 inclusive.

4. Composition according to any one of the preceding claims, characterized in that the quantity of nickel present in the active phase, relative to nickel and cobalt together, is between 10 and 60 % by weight.

5. Process for the preparation of a catalytic composition according to claim 1, characterized in that:

- in a first stage, the support is wetted with a solution of adhering agent,
- in a second stage, a catalytic solution or a suspension is prepared which contains various oxides or

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their precursors, and which is free from dopants, and which is then dried and calcined,

- in a third stage, the support is coated with the catalyst prepared in the second stage and with a solution of adhesive agent and dopants, and

- in a fourth stage, the composition obtained in the third stage is calcined.

6. Process for the preparation of α-β-unsaturated aldehydes by oxidation of olefins in the gas phase, characterized in that it is carried out in the presence of a catalytic composition according to any one of claims 1 to 4.

7. Process for the preparation of acrolein by oxidation of propylene in the gas phase, characterized in that it is carried out in the presence of the catalytic composition according to any one of claims 1 to 4.

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IN THE MATTER OF a Singapore Application corresponding to PCT Application PCT/FR95/00407

I, Andrew Harvey David SUMPTER BSc, c/o Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England, do solemnly and sincerely declare that I am conversant with the English and French languages and am a competent translator thereof, and that to the best of my knowledge and belief the following is a true and correct translation of the amended sheets of the PCT Application filed under No. PCT/FR95/00407.

Date: 15 August 1996

A. H. D. SUMPTER
For and on behalf of RWS Translations Ltd.

SG 9611508-4

* C L M S *

CLAIMS

1. Catalytic composition for the preparation of α-β-unsaturated aldehydes by oxidation of olefins, comprising a support coated with an active phase which is based on bismuth, molybdenum and/or tungsten, cobalt, nickel, iron, oxygen and is doped with phosphorus and at least one alkali metal element, characterized in that the said active phase representing from 15 to 33 % by weight of the catalytic composition, and the active phase has an atomic ratio 100 x (P + alkali metal elements)/Ni of between 0.9 and 10.

2. Composition according to the preceding claim, characterized in that the atomic ratio is between 0.9 and 7.

3. Catalytic composition according to any one of the preceding claims, characterized in that the atomic ratio of the alkali metal element to the phosphorus is from 0.3 to 3 inclusive.

4. Composition according to any one of the preceding claims, characterized in that the quantity of nickel present in the active phase, relative to nickel and cobalt together, is between 10 and 60 % by weight.

5. Process for the preparation of a catalytic composition according to claim 1, characterized in that:

- in a first stage, the support is wetted with a solution of adhering agent,

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* C L M S *

- in a second stage, a catalytic solution or a suspension is prepared which contains various oxides or their precursors, and which is free from dopants, and which is then dried and calcined,
- in a third stage, the support is coated with the catalyst prepared in the second stage and with a solution of adhesive agent and dopants, and
- in a fourth stage, the composition obtained in the third stage is calcined.

6. Process for the preparation of acrolein by oxidation of propylene in the gas phase, characterized in that it is carried out in the presence of the catalytic composition according to any one of claims 1 to 4.

7. Catalytic compositions having improved stability over time which are used for the oxidation of olefins to α-β-unsaturated aldehydes, characterized in that they contain nickel.

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- in a second stage, a catalytic solution or a suspension is prepared which contains various oxides or their precursors, and which is free from dopants, and which is then dried and calcined,
- in a third stage, the support is coated with the catalyst prepared in the second stage and with a solution of adhesive agent and dopants, and
- in a fourth stage, the composition obtained in the third stage is calcined.

6. Process for the preparation of acrolein by oxidation of propylene in the gas phase, characterized in that it is carried out in the presence of the catalytic composition according to any one of claims 1 to 4.

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