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**PAPER B
CHEMISTRY**

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93/B(C)/e

INSTRUCTIONS TO CANDIDATES

In this paper, you should assume that a European patent application for all the Contracting States comprising the appended documents * has been filed and that the European Patent Office has issued the annexed official communication.

You should accept the facts given in the paper and base your answers upon such facts. Whether and to what extent these facts are used is your responsibility.

You should not use any special knowledge you may have of the subject-matter of the invention, but are to assume that the prior art given is in fact exhaustive.

Your task is now to draft a full response to the official communication. The response should be a letter to the EPO, accompanied, if appropriate, by an amended set of claims. No amendments to the description should, however, be made.

The claims should afford the broadest protection possible while meeting the requirements of the Convention. In your letter of response you should set out your arguments in support of the patentability of the independent claim(s).

If your response includes a proposal to make any part of the application the subject of one or more divisional applications, you should in a note, clearly identify the subject-matter of the independent claim of such divisional application(s) and the justification for this. However, it is not necessary to draft the wording of the independent claim for the or each divisional application.

In addition to your chosen solution, you may – but this is not mandatory – give, in a note, the reasons for your choice of solution, for example, why you selected a particular form of claim, a particular feature for an independent claim, a particular piece of prior art as starting point or why you rejected or preferred some piece of prior art. Any such note should however be brief.

It is assumed that you have studied the examination paper in the language in which you have given your answer. If this is not so, please indicate on the front page of your answer in which language you have studied the examination paper. This always applies to candidates who – after having filed such a request when enrolling for the examination – give their answer in a language other than German, English or French.

Different sets of claims for those states which have made reservations under Article 167 (2) EPC are not required.

* These documents do not necessarily constitute the only or best solution to the task set in Paper A (Chemistry).

Description of the Application

This invention relates to catalytic compositions and to their use in a process for performing oxidative reactions of saturated or unsaturated hydrocarbons, particularly of olefins. Preferably the catalytic compositions are used in the ammoxidation of propene to acrylonitrile and the oxidative dehydrogenation of 1-butene to butadiene.

The catalytic compositions according to this invention make possible the preparation of the desired products at high rates and selectivities in good yields. Moreover, it is another advantage that these catalytic compositions can be easily prepared from known starting compounds by process steps familiar to the chemist or chemical engineer.

The oxidative reactions of olefins are in principle known. Reference can thus be made to Document I disclosing a specific antimony oxide based catalytic composition useful in the oxidative dehydrogenation of olefins to diolefins and to aromatic compounds. The known catalyst, optionally supported on refractory material, additionally contains iron and further activator elements. The document also refers to the use of the catalyst in the ammoxidation of olefins or in the oxidation of alcohols, e.g. of the butanols, to the corresponding aldehydes and carboxylic acids. This document also refers to the reaction conditions under which these reactions are generally carried out.

Document II describes the oxidation of unsaturated hydrocarbons such as α -olefins having up to 4 carbon atoms as well as of tert.-butanol with oxygen or oxygen containing gas mixtures to the corresponding unsaturated aldehydes, acids and/or conjugated dienes in the presence of a catalyst. It discloses the preparation of butadiene from 1-butene, and of methacrolein and methacrylic acid from isobutene.

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The catalyst of this document, supported or unsupported, consists essentially of mixed oxides of various main group and transition elements. In all cases the presence of Mo, Bi, Ni and Sb, of at least one metal selected from K, Rb, Cs and Tl and of at least one element selected from Se, Te, V, Ru, and Nb in specific amounts is mandatory.

The object of the present invention is to provide further improved catalytic compositions and to improve the known catalysed oxidative processes especially with respect to the induction period, the conversion of the olefin, the yield of the products, the selectivity of the reaction and the service life of the catalytic compositions.

The catalytic compositions of the present invention are defined by the general empirical formula (I):



wherein

A represents one or more elements selected from copper (Cu), vanadium (V), molybdenum (Mo) and/or tungsten (W),

D represents one or more activator elements selected from cobalt (Co) and/or bismuth (Bi),

Y is an alkali metal, and

a is 0.001 to 10, b is 0 to 10,

c is 10, d is 0.1 to 10,

e is 0.001 to 10, f is 0 to 0.01,

$a + b + d + e \leq 11$

x represents the number of oxygen atoms necessary to satisfy the valency requirements of the other elements present.

These compositions are particularly suitable for use in oxidative reactions of unsaturated and saturated hydrocarbons, preferably of olefins.

For the reason of simplification the above components A, D, Sb, Sn and Te are referred to as metals and their compounds as metal compounds, unless otherwise further specified.

The most promising compositions are those wherein at least two elements A of different groups of the periodic table are present. Very good results are obtained when a (or the total of a when more than one A element is present) is from 0.05 to 5, with best results in the range of 0.1 to 2.5. The values of the other indices in formula (I) can vary in the above ranges.

It should be noted that - as is known in the art - the composition of such catalysts is critical and that even minor modifications of the above catalytic compositions may result in insufficient activity or even total failure.

It is necessary that the starting metal compounds can be converted to the hydroxides or hydrated oxides by strong heating and to the oxides by calcination (i.e. intensive heating in the presence of oxygen). Thus, antimony or tin chloride may be converted to the oxide.

Elements which must in any case be absent in the final catalytic compositions are arsenic (As), selenium (Se) and halogens. Small amounts of alkali metals, i.e. up to 0.1 mole %, based on antimony, can be tolerated. Apart from this the catalytic compositions should be essentially free of any other components in any form. Such impurities should be strictly avoided or, if present, removed at the latest during calcination.

One possibility for achieving such pure compositions is to use starting compounds which already fulfil these requirements. Such sufficiently pure compounds are normally available on the market. On the other hand, it is possible to prepare suitable starting compounds according to generally known techniques. An example for the preparation of catalytic compositions according to the invention is given in this application. The steps taken in this

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example can be used in the preparation of the other compositions within the scope of this application as well, as will be obvious to a person skilled in the art.

5 These compositions can be used as such or supported on a suitable water-insoluble inert carrier. In either case the calcined compositions are crushed and ground to the desired particle size or granulated or shaped, e.g. to pellets, in the usual manner.

10 Suitable carriers which are well known in the art are finely divided refractory materials such as silica, alumina, zirconia or alumina-silica which can be used in amounts of up to 500% by weight of the catalytic compositions without any marked effect on the activity of the catalytic compositions. Therefore further
15 particulars in this respect are not necessary.

The exact working conditions to be met in the preparation of the catalytic compositions depend largely on the compounds involved. These conditions can easily be found and optimised by a person
20 skilled in this art.

The catalytic compositions of this invention can be used in oxidation reactions already known in the art, e.g. known from Document I, preferably in the oxidative dehydrogenation of 1-butene
25 to butadiene, and in the ammonoxidation (ammoxidation) of propene with ammonia to acrylonitrile.

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These reactions catalysed by the new catalytic compositions are carried out under the same or similar conditions as have been used up to now in these reactions, cf. e.g. Document I. Therefore it is not necessary to refer specifically to reaction parameters such as
5 temperatures, pressures, stoichiometric ratios of the reactants etc. which can be varied and optimised by the skilled chemical engineer in the usual manner and according to the specific requirements.

10 It can be said that the catalytic compositions of this invention produce the desired products in excellent yields at high rates and in excellent selectivities over long periods. One of the remarkable features of the catalytic compositions of the invention, especially when supported on an inert alumina carrier, is their short
15 induction period and in comparison to known catalysts their longer service life at an essentially constant activity.

In general, air will be used as an oxidising agent for economical and technical reasons. Thus, air offers the advantage that oxygen
20 is already mixed with inert diluents. In ammoxidation ammonia is used together with the oxidising agent.

Lower olefins, preferably α -olefins having 2 to 6 carbon atoms, are the preferred starting material in the reactions catalysed by the
25 catalytic compositions of this invention. In principle all hydrocarbons can be partly oxidised using these catalytic compositions. For practical reasons, the starting hydrocarbon, either pure or mixtures of such compounds, should be liquid or preferably gaseous under reaction conditions, thus allowing one
30 reliably to control concentration, residence time and selectivity.

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As already indicated above, air contains inert diluents which prevent overheating of the reactor and occurrences of hot spots within the reaction zone. Such detrimental reaction conditions reduce the selectivity and may even cause tarlike decomposition products to be formed which very quickly reduce or even destroy the activity of the catalytic compositions, thus reducing their service life, and require frequent shutdown of the plant. Moreover, frequent complicated and costly cleaning of those parts of the production plant which come into contact with the effluents including the reactor itself becomes inevitable. The catalytic compositions deactivated by such decomposition products are markedly more difficult to regenerate than catalysts not so contaminated.

Another aspect of this invention are improvements as regards regeneration of used catalytic material. The catalytic compositions of this invention can easily be regenerated almost to or to their initial activity, thus allowing their repeated use in preferably up to ten use/regeneration cycles. Remarkably good results were obtained when regenerated and fresh catalytic compositions are mixed in weight ratios of 95:5 to 70:30. Preferably, catalytic compositions different in their chemical constitution should not be mixed together because of sometimes less advantageous results.

The catalytic compositions are usually removed from the oxidative process when their activity declines by about 10%, sometimes even before. If the catalytic material shows a greyish discolouration due to carbon residues, these residues can be removed by initial calcination. The catalytic material is impregnated with aqueous ammonia (or an aqueous solution of an ammonium salt which decomposes upon heating, e.g. Hartshorn salt), dried and calcined. Process conditions for drying and calcination do not seem to be too critical and, in general, are the same as in the preparation of the initial catalytic compositions. Thus, the drying is carried out at

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a temperature of up to 150°C and the calcination at temperature more than 550 to 950°C. Working above 550°C is mandatory for achieving a good activity, while effectiveness is drastically reduced after calcination at above 950°C, presumably due to sintering or recrystallisation. The calcination time necessary can vary widely from 0.5 h to a day.

In order to achieve a satisfactory activity the catalytic material should preferably be saturated with the ammonia or ammonium compound. On the other hand, care should be taken that some component may be washed out resulting in insufficient activity of the catalytic compositions if too much aqueous solution is applied to the catalytic compositions. Before being calcined the fresh catalytic compositions can also be treated with ammonia or ammonium compound which often results in an even better activity although the composition and the structure of the catalysts do not appear to have changed in this treatment.

The following examples and tables demonstrate the excellent results obtainable in the conversion of propene to acrylonitrile and of 1-butene to butadiene and are intended to further explain the present invention. The examples and tables also illustrate the use of some known catalysts A, B and C. The yield refers to the ratio of moles of product to moles of starting hydrocarbon fed in. In the tables the service life of the catalysts is also given. This is the life of the catalyst up to the time when the activity has fallen by 5%.

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Example 1

$\text{Cu}_{1.06}\text{Mo}_{0.19}\text{Sb}_{10}\text{Sn}_{3.3}\text{Te}_{0.47}\text{O}_x$ (catalyst I)

74.96 g of Sb_2O_3 was oxidised by addition of about 3 times its
5 weight of concentrated nitric acid with stirring and heating at
reflux for about 5 h. The solution was diluted with 400 ml of
water, and then 20.35 g of granular tin were added incrementally to
this solution under heating and stirring during about 2.5 h until
the metallic tin had disappeared. The resulting slurry was
10 filtered, and some water was again added to the solids obtained to
form another slurry. 1.76 g of ammonium paramolybdate and 13.12 g
of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were dissolved in water and added to the slurry,
followed by a suspension of 3.88 g of TeO_2 in HNO_3 . The pH was
adjusted to 6 ± 2 using concentrated aqueous ammonia. Thereafter the
15 slurry was evaporated to a paste and then dried in a drying oven at
 130°C for about 20 h with frequent stirring during the first 4 h.
The dry powder obtained was again impregnated with ammonia, dried,
then denitrified by heating it to 290°C in air and further heating
it to 435°C for an additional 3 h. The composition was then
20 calcined in air at 820°C for 3 h, then cooled, crushed and ground
to an average particle size of between 500 and 850 μm .

In a similar way compositions having the empirical formulae of

$\text{Cu}_{2.07}\text{W}_{0.28}\text{K}_{0.01}\text{Sb}_{10}\text{Sn}_{1.9}\text{Te}_{0.57}\text{O}_x$ on Al_2O_3 (catalyst II) and
25 $\text{VBiSb}_{100}\text{Sn}_{40}\text{Te}_4\text{O}_x$ on SiO_2 (catalyst III) were prepared.

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Example 2

A fixed-bed reactor having an inner diameter of 16 mm and a length of 500 mm was packed with 30 ml of one of the above catalyst I, II or III or one of the known catalysts A ($\text{Sn}_1\text{Sb}_3\text{O}_x$), B ($\text{Sn}_1\text{Sb}_3\text{O}_x$ on SiO_2) or C ($\text{Cu}_{1.27}\text{Mo}_{0.23}\text{Sn}_4\text{Sb}_{10}\text{O}_x$) and heated in a molten salt bath comprising a mixture of equal amounts of sodium nitrite and potassium nitrate. The reactor was fed with a gas mixture of air, 1-butene and water vapour in the molar ratios air/1-butene = 5 and water/1-butene = 1.5 at a rate of 7.5 l per hour. The pressure in the reactor was approximately 0.1 MPa. The reaction temperatures and the conversion of the butene and the yield of butadiene are given in table 1.

Example 3

The catalyst I the activity of which had fallen by 7% was discharged from the reactor and regenerated in the following manner: A 34% aqueous ammonia solution was sprayed onto and impregnated into the agitated used catalyst (pore volume: 0.38 ml/g) at room temperature until no further ammonia was absorbed. Thereafter the temperature was gradually raised, and the catalyst was dried at 120°C for 16 h. This procedure was then repeated again. Thereafter the catalyst was calcined at 800°C for 5 h in air. This regenerated catalyst (identified as catalyst IV) was again used in the dehydrogenation reaction under the same conditions as described above. The butene conversion and the yield of butadiene are given in table 1.

Example 4

Example 2 was repeated with the modification that the regenerated catalyst IV of example 3 was mixed with additional fresh catalyst I of example 1 in a weight ratio of 9:1. The catalyst is named catalyst V in table 1.

Example 5

As shown in table 2 the catalysts of the previous examples and named as in table 1 were used in the ammoxidation of propene (AN = acrylonitrile). The molar ratio of oxygen in the air to the propene in the feed to the reaction vessel was 2.7:1. The molar ratio of the ammonia to the propene in the feed to the reactor was 4.6:1. Water vapour was added to the feed in a molar ratio to the propene of 1.4:1.

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Table 1

	Catalyst	Calcination (°C)	Reaction (°C)	Conversion (% butene)	Yield (%butadiene)	Service life (days)
	A	800	380	83	78.0	79
	B	820	380	84	81.2	76
	C	800	370	88	82.1	99
15	I	820	370	93	87.5	108
	II	820	370	96	88.9	109
20	III	800	370	90	84.4	101
	IV	800	370	92	86.9	106
	V		370	93	86.9	108

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Table 2

	Catalyst	Reaction (°C)	Conversion (%propene)	Yield (%AN)	Yield (%HCN)	Service life (days)
	A	430	87	51.1	6.2	74
	B	460	89	61.5	7.3	72
	C	460	90	59.1	4.3	75
	I	460	96	73.7	5.2	92
30	II	460	92	71.4	5.4	89
	III	460	92	69.7	6.1	89
	IV	460	95	73.5	5.1	91
35	V	460	96	73.6	4.7	94

Claims

1. Catalytic compositions defined by the general empirical formula (I):



wherein

A represents one or more elements selected from copper (Cu), vanadium (V), molybdenum (Mo) and/or tungsten (W),

D represents one or more activator elements selected from cobalt (Co) and/or bismuth (Bi),

Y is an alkali metal,

a is 0.001 to 10,

b is 0 to 10,

c is 10,

d is 0.1 to 10,

e is 0.001 to 10,

f is 0 to 0.01,

a + b + d + e ≤ 11; and x represents the number of oxygen atoms necessary to satisfy the valency requirements of the other elements present.

2. Catalytic compositions of claim 1 which are supported by an inert refractory material.
3. Process for the preparation of catalytic compositions of claim 1 or claim 2 characterised in that the components of the catalytic compositions in the form of oxides or compounds of the elements involved which can be converted into oxides, hydroxides or hydrated oxides by heating and calcination are mixed together, optionally with the support, and then calcined at temperatures of from about 550 to 950°C.
4. Use of the catalytic compositions of claims 1 or 2 in the oxidative reactions of unsaturated or saturated hydrocarbons.

5. Method of regeneration of the catalytic compositions used in reactions of claim 4 characterised in that they are removed from the reactor, then impregnated with concentrated aqueous ammonia until saturation, dried at a temperature of up to 150°C and calcined at temperatures of from 550 to 950°C.

Communication

1. Document III anticipates catalyst I. The known catalyst was prepared by mixing oxides of the elements involved in aqueous slurry and by then drying and calcining the solid residue at 650 to 850°C. The catalyst was used in an oxidative reaction of saturated or unsaturated hydrocarbon compounds. The document specifically refers to the oxydehydrogenation of α -olefins to the corresponding dienes by using this specific or slightly different catalysts. Therefore the subject matter of claims 1 to 4 is not new, Art. 54(1) and (2) EPC.
2. Document IV describes another process for the preparation of butadiene by oxydehydrogenation of 1-butene by means of an oxidic catalyst. It also refers to the use of the catalyst in the ammoxidation of α -olefins to unsaturated nitriles. The reactions are carried under the conditions set out in your application. The catalyst and the procedure described in the example of this document appear to correspond to your catalyst III and its preparation. Therefore the subject matter of this document anticipates your claims 1 to 4, Art. 54(1) and (2) EPC.
3. Document V relates to a further catalyst for the ammoxidation of propene. The catalyst appears to be at least similar to yours. This is evident especially from the passage starting in paragraph 2 of page 2 of this document where reference is made to a specific catalyst and its use. This specific catalyst appears to be identical to your catalyst II. Having regard to this document claims 1 to 4 do not meet the requirements of Art. 52 (1) and 54(1) and (2) EPC either.

4. The example of Document IV and the paragraph of Document V referring to the use of a specific catalyst both disclose the regeneration of such catalysts according to the method of your claim 5 (treatment with ammonia or ammonium salt and subsequent calcination). Therefore claim 5 does not meet the novelty requirement of Art. 52(1) and 54(1) and (2) EPC either.
5. Documents I and II as referred to in your application both appear to indicate that enhancing oxidative reactions by means of oxidic catalysts of the kind presently claimed in your application has been common knowledge.
6. It is not at present apparent which part of the application could serve as a basis for a new, allowable claim. Should you nevertheless regard some particular matter as patentable an independent claim including such particular matter should be filed taking account of Rule 29(1) EPC. You should also indicate in the letter of reply the difference vis à vis the state of the art and the significance thereof. Thus, you should explain your invention in such terms that the problem to be solved by each independent claim with respect to the closest prior art and the solution found can be understood (cf. the requirements of Rule 27 (1) (b) and (c) EPC).

DOCUMENT III (State of the Art)

A catalyst consisting of mixed oxides of Cu, Mo, Sb, Sn and Te in atomic ratios of 106:19:1000:330:47 is used as a catalyst in the oxidation of n-butanol to butyric acid in the gas phase. The reaction is carried out in a fluid bed reactor at temperatures of 380 to 425°C. The yield is about 87% depending on the working conditions with a selectivity of approximately 64%.

The catalyst is prepared by mixing the oxides of the components with sufficient water to form a slurry. After filtration the solid residue is dried and then calcined at 650 to 850°C (the temperature being gradually raised during this process) for 12 h. The calcined material is ground and then formed into pellets.

Similar compositions of the same elements with slightly different compositions have also been tested, but the composition according to the above formula within a variation of the ratios of less than $\pm 0.1\%$ has been found to be the best since it can be used for longer periods without significant decrease of its activity.

Similar results as regards activity and service life could also be found when using the above catalysts as such or supported on alumina in the oxydehydrogenation of α -olefins to the corresponding conjugated dienes.

The catalyst can be regenerated by burning deposits which inevitably form on the catalyst during the above oxidation reaction and which tend to reduce the activity of the catalyst. The regeneration is carried out at temperatures of around 900°C.

DOCUMENT IV (State of the Art)

An olefin having 4 to 10 carbon atoms can be dehydrogenated with molecular oxygen, usually added as air, in the presence of a catalyst. The oxygen is preferably used in amounts of about 0.2 to 6 moles per mole of olefin in order to obtain best results. Ratios
5 outside this range can also be used. The reactants can be diluted, e.g. with steam.

Preferred reactants are 1-butene, which is converted to butadiene, or isopentene giving isoprene. It should be noted that the catalyst
10 can also be used in other oxidation reactions of olefins, e.g. in the ammoxidation of α -olefins which yields unsaturated nitriles.

The reactions are usually carried out at temperatures of between about 200 and about 600°C, with temperatures of about 300 to about
15 500°C being preferred. The reactants can be passed over the catalyst at an apparent contact time as low as a fraction of a second to 20 seconds or more. The reaction can be conducted in a fluid-bed or fixed-bed reactor at atmospheric pressure or above or
20 at subatmospheric pressure. Under these conditions the present invention gives high yields of diolefins from the corresponding olefin.

Example

25 An aqueous slurry containing 1.17 g of $(\text{NH}_4)_4\text{VO}_3$, 2.60 g of $\text{Bi}(\text{OH})_3$, 1652 g of 40% Nalco^(R) silica sol and 291.5 g of Sb_2O_3 was prepared. Separately, 90.25 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 9.11 g of
30 $(\text{NH}_4)_2\text{TeO}_4$ were dissolved in water. Then the slurry and the solution were intimately mixed together, and the water was removed

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overnight by evaporation in an oven at 110°C. The dry material obtained was saturated twice with an aqueous solution of ammonium carbonate with drying after each impregnation. Thereafter the solid material obtained was heated to 290°C for 3 h and to 570°C for
5 another 16 h. The catalyst which had the empirical formula $V_{0.1}Bi_{0.1}Sn_4Sb_{10}Te_{0.4}O_x$, supported on SiO_2 , was ground and formed into pellets.

Using an air/butene feed having a molar ratio of oxygen to olefin
10 of 31, a temperature of 350°C and a contact time of 1 second, the conversion was 71.2%, the selectivity 97% and the yield of butadiene was 68.9%. The catalyst could be easily regenerated by treatment with aqueous ammonia and calcination to obtain practically the same results as with the fresh catalyst.

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This catalyst gave also excellent results in the ammoxidation of propene to acrylonitrile (up to 70%) with low contents of hydrogen cyanide (as low as 6%).

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DOCUMENT V (State of the Art)

This invention relates to a process for the production of a composite oxide catalyst of the formula



wherein

- 5 X represents K, Rb, Cs, Cu and/or Tl,
Y represents B, Sn, P, As, Mo and/or W,
Z represents selenium and/or tellurium,
Sp represents an inert support,
a - j represent atomic ratios, respectively,
10 a is 100, b is 0 to 50, c is 0 to 50, d is 0 to 50, e is 0 to 30, f is 0 to 6, g is 0.1 to 40, h is 0 to 50, i is 0 to 50, j is 0 to 500, and x is a numeral which satisfies the oxidation states of the other elements, with the proviso that b+c+d+e+f+h+i is >0 and ≤50 and to its use in ammoxidation of propene to produce acrylonitrile.

15 The preparation of the catalyst according to this invention will now be described in more detail.

Oxides, e.g. bismuth oxide, bismuth oxycarbonate, antimony oxide
20 and/or inert carriers such as silica and alumina in finely divided powdery form are suspended in a small amount water to obtain a stirrable suspension. Then aqueous solutions of salts, preferably nitrates, of cobalt, nickel, iron, sodium, potassium, rubidium, cesium, copper, tin and/or thallium are mixed therewith. Thereafter
25 boron, phosphorus, arsenic, molybdenum, tungsten, selenium and/or

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tellurium compounds are added, preferably in the form of aqueous solutions. The slurry thus obtained is stirred thoroughly and then dried. The dry product in the form of granules or cake is subjected to a heat treatment at a temperature of 270 to 350°C to convert the salts into the corresponding oxides.

In a further thermal treatment the product is subjected to temperatures of 450 to 650°C for 1 to 16 h in non-reducing atmosphere, preferably in the presence of molecular oxygen, particularly in air. The resulting catalyst can be ground and/or pelletised as desired.

Thus, a catalyst containing Sb:Sn:Cu:W:K:Te in atomic ratios of 100:19:20.7:2.8:0.1:5.7 and supported on Al_2O_3 was charged into a stainless steel reaction tube having an internal diameter of 15 mm, and propene is oxidised by passing a gas feed comprising 10 vol.% of propene, 17 vol.% of steam, 19 vol.% of ammonia and 54 vol.% of air at atmospheric pressure with a contact time of 4.8 seconds through the reaction tube.

At a reaction temperature of 440°C, the following results were obtained:

Propene conversion 91%,
acrylonitrile yield 70.8%.

After regeneration of the used catalyst by impregnation with ammonium carbonate (Hartshorn salt) and calcination at 600°C a conversion of 89%, a selectivity of 87% and an acrylonitrile yield of 68.3% were obtained.

DOCUMENT I (State of the Art)

(This document is identical to Document I of Paper A)

This invention relates to an antimony oxide based catalyst composition useful in the oxidative dehydrogenation of olefins to diolefins and to aromatic compounds.

5 The catalyst can be defined by the empirical formula



wherein α is 50 to 98, β is from >0 to <50 , δ is 0.001 to 25 and ϵ is a number taken to satisfy the average valencies of antimony, iron and of component X in the catalyst; $\alpha + \beta + \delta$ being 100.

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Activator elements X are certain transition and/or main group elements which form compounds in more than one oxidation state. These elements are arsenic (As), bismuth (Bi), cobalt (Co), copper (Cu), molybdenum (Mo), nickel (Ni), selenium (Se), tellurium (Te),
15 tin (Sn), tungsten (W) and vanadium (V). These activators are preferably in the form of their oxides in amounts from about 0.01 to about 20% by weight, more preferably 1 to 10% by weight, based on the weight of the total of the catalyst, exclusive of any support, if present.

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The activator element can be incorporated into the base catalyst by co-precipitation, by impregnation or by other methods.

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The catalyst which may be supported by refractory materials such as silica, ilmenite or alumina very effectively enhances the reaction of olefins such as butenes with air to alkadienes such as butadiene or to aldehydes and carboxylic acids such as methacrolein and methacrylic acid. It has also proven to be highly effective in

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ammonoxidation of olefins or in the oxidation of alcohols, e.g. the butanols, to the corresponding aldehydes and carboxylic acids

The catalyst is used under reaction conditions well known in the art. Therefore it is not necessary to specify these reaction parameters such as temperatures, pressures, oxidising agents, stoichiometric ratios of the reactants, presence or absence of diluents, design and size of the reaction apparatus (e.g. stirred vessels, fixed-bed or fluid-bed gas phase reactors, tube reactors, loop reactors, cascade reactors), feeding in of the reactants, contact time, processing of the effluents and recovery of the products which can be varied and optimised by the skilled chemical engineer in the usual manner and according to the requirements.

15 Example

A fixed-bed reactor having an inner diameter of 20 mm and a length of 1000 mm was packed with 50 ml of a catalyst having the formula $Sb_{30}Fe_{13}Co_{0.23}O_e$ and heated in a molten salt bath comprising a mixture of equal amounts of sodium nitrite and potassium nitrate. The reactor was fed with a gas mixture of air, 1-butene and water vapour so that the molar ratio of air to 1-butene was 6:1 and that of water to 1-butene was 1.7 at a rate of 10 l per hour. The pressure in the reactor was approximately 0.1 MPa. The reaction temperature was kept at 410°C. The conversion of the butene was 76% and the yield of butadiene was 72%.

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DOCUMENT II (State of the Art)

(This document is identical to Document II of Paper A)

Unsaturated hydrocarbons such as α -olefins having up to 4 carbon atoms as well as tert.-butanol can be converted with oxygen or oxygen containing gas mixtures at temperatures of 200 to 450°C to the corresponding unsaturated aldehydes, acids and/or conjugated dienes in the presence of a catalyst. Thus butadiene can be produced from 1-butene, and methacrolein and methacrylic acid from isobutene in high yields.

The catalyst consists essentially of



wherein

X denotes at least one metal selected from K, Rb, Cs and Tl,

Y denotes at least one element selected from Se, Te, V, Ru and Nb,

15 a to j are atomic ratios of each component such that

a is 0.5 to 50

b is 0.01 to 60

c is 0 to 60

d is 0.01 to 60

e is 0 to 100

f is 0.0005 to 20

g is 1

h is 0 to 100

20 i is 0.0005 to 20

j is a value corresponding to

the valencies of the elements in the catalyst and wherein, when Y

is at least one metal selected from V, Ru and Nb, e is 0.

The preparation of the catalyst can be accomplished by methods well known in the art. Any oxide of the elemental components of the catalyst can be used as a starting material or any compound of the elements which is converted to an oxide when it is calcined. Suitable sources of Mo include ammonium molybdate, molybdic acid or

30

35

molybdenum trioxide. Suitable sources of Sb include the oxides, hydrated oxides and chlorides thereof.

The catalysts may be used as they are or supported on such known carriers as silica, alumina, silica-alumina or silicon carbide.

The reaction can be carried out in fluid bed or fixed bed, in stirred vessels or static mixers either in gas phase or in liquid phase, e.g. in an inert solvent. The oxidising agent may be oxygen or an oxygen-containing gas feed. Air is preferred for economical reasons. The feed is preferably diluted with an inert gas such as nitrogen, steam or carbon dioxide. The reaction may be carried out at ambient pressure conditions or under elevated or reduced pressures, preferably at about 0.1 MPa.

Examples

Sb_2O_3 , $(NH_4)_2TeO_4$ and $SnCl_2$ were homogeneously mixed in aqueous dispersion with at least some of $BiONO_3 \cdot H_2O$, $CsNO_3$, KNO_3 , $(NH_4)_2MoO_4$, $VOCl_3$, $Ni(NO_3)_2 \cdot 6H_2O$ and SiO_2 . The mixtures were then dried at elevated temperatures and then calcined with agitation at 560 to 950°C under an atmosphere of air. The product was then ground to particle sizes of 0.6 to 0.8 mm and pelleted to give the catalysts identified in table 1 (Catalysts A to F are added for comparison).

The catalysts obtained were then packed in a fixed bed reaction vessel and maintained at 360°C. A gas mixture of 5 vol.% isobutene, 12 vol.% oxygen, 48 vol.% nitrogen and 35 vol.% steam was fed into the reactor. The results are given in table 2.

In table 3 the results are given of a conversion of 1-butene to butadiene under similar conditions.

As is demonstrated in these examples the yield of the different products is highly dependent on the catalyst composition.

Table 1

Catalyst	Composition
A	$\text{Mo}_3\text{Bi}_5\text{Ni}_2\text{Sb}_{200}\text{Sn}_{40}\text{Te}_{25}\text{V}_2\text{O}_j$ on SiO_2
B	$\text{Mo}_4\text{Bi}_6\text{Cs}_1\text{Sb}_4\text{Sn}_3\text{Te}_1\text{V}_1\text{O}_j$
C	$\text{Mo}_4\text{Bi}_1\text{Ni}_2\text{Cs}_1\text{Sb}_5\text{Sn}_4\text{Te}_5\text{O}_j$ on Al_2O_3
D	$\text{Mo}_3\text{Ni}_2\text{Sb}_{200}\text{Sn}_{40}\text{Te}_{25}\text{V}_2\text{O}_j$ on SiO_2
E	$\text{Mo}_{0.5}\text{Ni}_{0.15}\text{K}_{0.035}\text{Sb}_1\text{Sn}_{0.2}\text{Te}_{0.025}\text{V}_{0.06}\text{O}_j$ on SiO_2
F	$\text{W}_{0.5}\text{Bi}_{0.075}\text{Ni}_{0.15}\text{K}_{0.035}\text{Sb}_1\text{Sn}_{0.2}\text{Te}_{0.025}\text{V}_{0.06}\text{O}_j$
1	$\text{Mo}_{20}\text{Bi}_1\text{Ni}_8\text{Cs}_{0.4}\text{Sb}_1\text{Sn}_{24}\text{Te}_{1.4}\text{O}_j$ on SiO_2
2	$\text{Mo}_{0.5}\text{Bi}_{0.075}\text{Ni}_{0.15}\text{K}_{0.035}\text{Sb}_1\text{Sn}_{0.2}\text{Te}_{0.025}\text{V}_{0.06}\text{O}_j$ on SiO_2
3	$\text{Mo}_2\text{Bi}_{0.4}\text{Fe}_{0.4}\text{Ni}_{1.2}\text{Cs}_{0.16}\text{Sb}_1\text{Sn}_{1.8}\text{Te}_{0.5}\text{V}_{0.1}\text{O}_j$ on SiO_2

Table 2

Catalyst	Calcination ($^{\circ}\text{C}$)	Total Yield (%) of methacrolein and methacrylic acid
A	860	75.7
B	860	71.3
C	880	77.1
D	850	74.7
E	840	72.9
F	850	74.6
1	840	83.7
2	900	84.3
3	860	82.9

Table 3

Catalyst	Reaction ($^{\circ}\text{C}$)	Butadiene yield (%)
D	340	67
E	340	72
F	345	70
1	350	75
2	340	78
3	350	76