EUROPEAN QUALIFYING EXAMINATION 1993

PAPER A
CHEMISTRY

This paper comprises:

INSTRUCTIONS TO CANDIDATES

You are to assume that you have received the annexed letter from your client including a description of an invention for which he wishes you to obtain a European patent together with references to the most pertinent prior art known to your client.

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 to draft an independent claim (or claims) offering the applicant the broadest protection possible while at the same time having a good chance of succeeding before the EPO. In drafting your claim(s) you should bear in mind the need for inventive step over the prior art indicated, the requirements of the Convention, in particular as to the form of claims, and the recommendations made in the Guidelines for Examination in the EPO. Dependent claims should also be drafted so as to enable you to fall back upon them should the independent claim(s) fail and should be kept to a reasonable number.

You are also expected to draft an introduction, i.e. that part of the description which precedes the examples or the explanation of the drawings. The introduction should be sufficient to provide support for the independent claim(s). In particular, you should consider the advisability of mentioning advantages of the invention in the introduction.

You are expected to draft claims and an introduction for one European patent application only. This application should meet the requirements of the Convention as to unity. If you would in practise seek to protect further inventions by filing one or more separate applications, you should, in a note, clearly identify the subject-matter of the independent claim of such separate application(s). However, it is not necessary to draft the wording of the independent claim for the or each separate 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.

PAPER A/1993 (Chemistry)

Client's Letter

We have developed new catalytic compositions for performing oxidative reactions of saturated or unsaturated hydrocarbons, particularly of olefins. Examples of such reactions are the ammoxidation of propene to acrylonitrile and the oxidative dehydrogenation of 1-butene to butadiene.

Our invention makes possible the preparation of the desired products, especially of acrylonitrile and butadiene, at high rates and selectivities in good yields. Moreover, it is another advantage that our catalytic compositions can be easily prepared from known starting compounds by process steps familiar to the chemist or chemical engineer.

Therefore we ask you to prepare and file a European patent application for this invention. We are interested in a strong protection as broad as possible based on the information in this letter. As you certainly know, the composition of such catalysts is critical and even minor modifications thereof may result in insufficient activity or even in total failure.

Our main interest is directed to the catalytic compositions (catalysts) as such, which we intend to sell to customers, and, additionally, also - as regards their propene and 1-butene feedstocks - to the above cited two reactions.

Please find enclosed copies of two prior art documents which should be of interest in the preparation of the application.

Our catalytic compositions can best be defined by the general empirical formula (I):

$$A_a D_b Sb_c Sn_d Te_e O_x$$

wherein

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

whereby

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, $a + b + d + e \leq 11$
x represents the number of oxygen atoms necessary to satisfy the valency requirements of the other elements present.

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.

Certain amounts of so-called activator elements can be incorporated in our catalytic compositions as component D. Reference can be made to Document I which discloses such activator elements (activator elements X).

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 our catalytic compositions is included in this letter. The steps taken in this example can be used in the preparation of the other compositions of our invention as well.

Our 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.

Suitable carriers which are well known in the art are finely divided refractory materials such as silica, alumina, zirconia or alumina silica. They can be used in amounts of up to 500 % by weight based on our compositions without any marked effect on the activity of the catalytic compositions. It seems to us that further 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 skilled in this art.

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

These reactions catalysed by our 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 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.

It can be said that our catalytic compositions produce the desired products in excellent yields at high rates and in excellent selectivities over long periods. One of the remarkable features of our catalytic compositions, especially when supported on an inert alumina carrier, is their short 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 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 our compositions, however, in principle all hydrocarbons can be partly oxidised using our 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 reliably to control concentration, residence time and selectivity.

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.

Our catalytic compositions can easily be regenerated almost to or to their initial activity, thus allowing their repeated use in preferably up to ten use/-regeneration cycles. We obtained remarkably good results when mixing regenerated and fresh catalytic compositions in weight ratios of 95:5 to 70:30. Preferably, 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 a temperature of up to 150°C and the calcination at temperatures of 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 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 be changed by this treatment.

Please find enclosed some examples and tables demonstrating the excellent results in the conversion of propene to acrylonitrile and of 1-butene to butadiene. The examples and tables also illustrate the use of some known catalysts **A**, **B** and **C**.

These examples should further clarify any questions remaining open. 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%.

Example 1

$Cu_{1.06}Mo_{0.19}Sb_{10}Sn_{3.3}Te_{0.47}O_x$ (catalyst I)

74.96 g of Sb_2O_3 was oxidised by addition of about 3 times its 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 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 $Cu(NO_3)_2 \cdot 3H_2O$ 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 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 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 $Cu_{2.07}W_{0.28}K_{0.01}Sb_{10}Sn_{1.9}Te_{0.57}O_x$ on Al_2O_3 (catalyst II) and $VBiSb_{100}Sn_{40}Te_4O_x$ on SiO_2 (catalyst III) were prepared.

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** ($Sn_1Sb_3O_x$), **B** ($Sn_1Sb_3O_x$ on SiO_2) or **C** ($Cu_{1.27}Mo_{0.23}Sn_4Sb_{10}O_x$) 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

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.

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
I	820	370	93	87.5	108
II	820	370	96	88.9	109
III	800	370	90	84.4	101
IV	800	370	92	86.9	106
V		370	93	86.9	108

Table 2

Catalyst	Reaction (°C)	Conversion (%propene)	Yield (%AN)	(%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
II	460	92	71.4	5.4	89
III	460	92	69.7	6.1	89
IV	460	95	73.5	5.1	91
V	460	96	73.6	4.7	94

DOCUMENT I (State of the Art)

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

The catalyst can be defined by the empirical formula

$$Sb_{\alpha}Fe_{\beta}X_{\delta}O_{\epsilon}$$

wherein α is 50 to 98, ß is from >0 to <50, δ is 0.001 to 25 and ϵ is a number taken to satisfy the average valencies of antimony and iron in the catalyst; α + ß + δ being 100.

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), 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.

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

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 ammonoxidation of olefins or in the oxidation of alcohols, e.g. of 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.

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 $Sb_{30}Fe_{13}Co_{0.23}O_{\epsilon}$ 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 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%.

DOCUMENT II (State of the Art)

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

$$Mo_a Bi_b Fe_c Ni_d Co_e X_f Sb_g Sn_h Y_i O_j,$$

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

The catalyst components 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, $(NH_4)_2\ TeO_4$ 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	$Mo_3Bi_5Ni_2Sb_{200}Sn_{40}Te_{25}V_2O_j$ on SiO_2
B	$Mo_4Bi_6Cs_1Sb_4Sn_3Te_1V_1O_j$
C	$Mo_4Bi_1Ni_2Cs_1Sb_5Sn_4Te_5O_j$ on Al_2O_3
D	$Mo_3Ni_2Sb_{200}Sn_{40}Te_{25}V_2O_j$ on SiO_2
E	$Mo_{0.5}Ni_{0.15}K_{0.035}Sb_1Sn_{0.2}Te_{0.025}V_{0.06}O_j$ on SiO_2
F	$W_{0.5}Bi_{0.075}Ni_{0.15}K_{0.035}Sb_1Sn_{0.2}Te_{0.025}V_{0.06}O_j$
1	$Mo_{20}Bi_1Ni_8Cs_{0.4}Sb_1Sn_{24}Te_{1.4}O_j$ on SiO_2
2	$Mo_{0.5}Bi_{0.075}Ni_{0.15}K_{0.035}Sb_1Sn_{0.2}Te_{0.025}V_{0.06}O_j$ on SiO_2
3	$Mo_2Bi_{0.4}Fe_{0.4}Ni_{1.2}Cs_{0.16}Sb_1Sn_{1.8}Te_{0.5}V_{0.1}O_j$ on SiO_2

Table 2

Catalyst	Calcination (°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 (°C)	Butadiene yield (%)
D	340	67
E	340	72
F	345	70
1	350	75
2	340	78
3	350	76