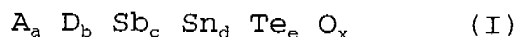


Candidate's examination paper (Examination paper A/1993 Chemistry)

CLAIMS

1. A catalytic composition of 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,

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

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

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

2. A composition as claimed in claim 1 wherein at least two elements A of different groups of the periodic table are present.
3. A composition as claimed in claim 1 or claim 2 wherein when one element A is present a is from 0.05 to 5 and when more than one element A is present, the total of a for each such element is from 0.05 to 5.
4. A composition as claimed in claim 3 wherein a is from 0.1 to 2.5.
5. A composition as claimed in any one of the preceding claims wherein D is selected from Bismuth (Bi), Cobalt (Co), Copper (Cu), Molybdenum (Mo), Nickel (Ni), Tellurium (Te), Tin (Sn), Tungsten (W) and Vanadium (V).
6. A composition of formula I as claimed in claim 1 being
- $$Cu_{1.06} Mo_{0.19} Sb_{10} Sn_{3.3} Te_{0.47} O_x$$
7. A composition of formula I as claimed in claim 1 being
- $$Cu_{2.07} W_{0.28} K_{0.01} Sb_{10} Sn_{1.9} Te_{0.57} O_x$$
8. A catalytic composition of formula
- $$V Bi Sb_{100} Sn_{40} Te_4 O_x$$

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9. A composition as claimed in any one of the preceding claims supported on an inert carrier.
10. A composition as claimed in claim 9 wherein the carrier is alumina.
11. A process for the preparation of a composition as claimed in any one of claims 1 to 8 said process comprising drying and calcination of the components in the form of their oxides.
12. A process as claimed in claim 11 wherein the oxides of the component elements are formed during the reaction.
13. A process as claimed in claim 11 or claim 12 wherein the components when combined are treated with ammonia or an ammonium compound prior to calcination.
14. Use of a catalytic composition as claimed in any one of claims 1 to 10 as a catalyst for oxidation of lower olefins.
15. A process for oxidative reactions of hydrocarbons characterised in that a catalytic composition as claimed in any one of claims 1 to 10 is employed.
16. A process as claimed in claim 15 for the oxidative reaction of olefins.
17. A process as claimed in claim 16 for the oxidation of C₂-C₆ olefins.
18. A process as claimed in claim 15, claim 16 or claim 17 for the ammoxidation of propene.
19. A process as claimed in claim 15, claim 16 or claim 17 for the oxidative dehydrogenation of 1-butene.
20. A process for the regeneration of a catalytic composition as claimed in any one of claims 1 to 10 wherein said composition is impregnated with ammonia or an aqueous solution of an ammonium salt, dried and calcinated.
21. A process as claimed in claim 20 wherein said drying is at a temperature of up to 150°C.
22. A process as claimed in claim 20 or claim 21 wherein calcination takes place at a temperature of from 550 to 950°C.

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23. A catalytic product comprising a mixture of regenerated and fresh catalytic compositions as claimed in any one of claims 1 to 10 in a weight ratio of 95:5 to 70:30 wherein said regenerated and fresh compositions have the same chemical constitution.

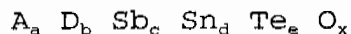
New catalytic composition and use thereof

The present invention relates to novel catalytic compositions and their use in oxidative reactions of olefins. The invention also relates to a process for regeneration of these compositions.

Antimony containing catalysts are known for the oxidative reaction of certain hydrocarbons. Thus Document I describes catalysts for the oxidative dehydrogenation of olefins, particularly of butene to butadiene and Document II describes both the above reaction and the oxidation of isobutene to methacrolein and methacrylic acid. Problems with the known catalysts are that they do not give high yields of reaction products and have short lifetimes.

We have now found that these problems can be solved by the use of novel catalytic compositions.

Thus according to one aspect, the present invention provides catalytic compositions of 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 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 ≤ 11

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

The activator element D maybe selected from Bi, Co, Cu, Mo, Ni, Te, Sn, W + V as described in Document I.

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We have found that compositions according to the above formula are catalytically active to achieve high rates and selectivity and good yield of products thereby solving certain problems of the prior art catalysts.

In particular, compounds of the above formula wherein at least two elements A of different groups of the periodic table are present are particularly good catalysts. 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.

Although the compositions may additionally comprise other elements 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. However, elements which must in any case be absent in the final catalytic compositions are arsenic (As), selenium (Se) and halogens.

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.

The compositions of the invention may be prepared by known techniques such as these described in Document II 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.

We have however found that pretreatment of the composition with ammonia or an ammonium compound prior to calcination produces catalysts having particularly high activity. The starting materials must be able to 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.

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Preferably, the catalytic compositions should be free of impurities. This can be achieved by the use of 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. Otherwise, impurities are removed during the calcination reaction.

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 ammonoxidation 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

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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.

A particular advantage of the catalysts of the invention is that they 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 about 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.

The invention will now be described with reference to the following examples.

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Note to examiner

Justification for claims.

1. I note that (p. 1 of client's letter) composition is critical and therefore I have not departed from the formula provided, although I note that certain elements for D also appear as options for A.
2. Catalyst III (p. 8 of letter) is not within the definition of formula I [since $b=100 + d=40$] but since it is part of invention, I have put it as an independent claim.
3. In definition of X, I've excluded As + Se which are given in I since client says at p. 3 that they must not be in the composition.
4. None of the compositions specifically recited in prior art I or II fall within the definition of formula I, therefore, no disclaimer etc. needed for claim 1[(...) decision where multiple options for substituents, only overlap possible is in specifically named compounds].
5. Analogy processes for patentable end products are allowable (Guidelines), hence my claim 11.
6. Regeneration process seems generally new, although I have limited it to the compositions of the invention since there is no indication that it is any more widely applicable.