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(64) **Process for forming multicomponent oxide complex catalysts.**

(57) **Process for forming multi-component oxide catalysts.**
According to the invention the key catalytic phase of the catalyst is preformed and the elements of the host-catalyst phase are added together or separately. The key catalytic phase contains a molybdate or a tungstate of Bi, Te, Sb, Sn Cu or mixtures thereof.

A representative catalyst is

50% $[\text{Bi}_2\text{Mo}_3\text{O}_{12}] \frac{1}{2} [\text{K}_{0.1}\text{Ni}_{2.5}\text{Co}_{4.5}\text{Fe}_3\text{P}_{0.5}\text{Mo}_{10.5}$

Ox] + 50% SiO_2

In the production of this catalyst a preformed bismuth molybdate slurry is added to a host-catalyst slurry. The mixture was then dried, calcined, ground and calcined once again.

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Title

Process for forming multi-
component oxide complex
catalysts.

The present invention relates to catalysts
useful in the oxidation and/or ammoxidation of
olefins. More specifically, the present invention
relates to a novel process for producing oxidation
5 and/or ammoxidation catalysts having superior
properties.

It is well known that olefins can be
oxidized to oxygenated hydrocarbons such as un-
saturated aldehydes and acids, for example, acro-
10 lein and methacrolein, and acrylic and methacrylic
acids. It is also well known that olefins can be
ammoxidized to unsaturated nitriles such as acryloni-
trile and methacrylonitrile. The value of such
oxygenated hydrocarbons and unsaturated nitriles is
15 generally well recognized with acrylonitrile being
among the most valuable monomers available to the
polymer industry for producing useful polymeric
products.

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Various catalytic processes are known for the oxidation and/or ammoxidation of olefins. In such processes it is common to react an olefin or an olefin-ammonia mixture with oxygen in the vapour phase in the presence of a catalyst. For the production of acrolein and acrylonitrile, propylene is generally used as the olefin reactant and for the production of methacrolein and methacrylonitrile, isobutylene is generally used as the olefin reactant.

Many different catalysts have been disclosed as useful in the oxidation and ammoxidation of olefins. Examples of, such catalysts are those disclosed in United States Patents, 3,882,159 and 3,746,657, US Patent Application Serial Number 748,609, filed December 7, 1976. Catalysts based on bismuth and molybdenum, that is bismuth molybdate catalysts, promoted with various additional elements such as iron, cobalt, nickel, potassium, phosphorus, chromium and manganese demonstrate particular utility in these reactions.

Bismuth molybdate catalysts have been prepared in the past by a number of different techniques. For example, Example III of U.S. 3,746,657 shows a method of preparation which comprises forming a mixture of potassium hydroxide, ammonium molybdate and silica, adding to the mixture phosphoric acid, solutions in nitric acid of the nitrates of cobalt, iron, nickel and bismuth, and more silica to form a slurry, then spray drying and calcining to form the catalyst. US Application Serial Number 748,609 discloses a

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catalyst preparation technique in which an aqueous solution of cobalt nitrate and nickel nitrate, an aqueous solution of potassium nitrate and iron nitrate, an aqueous nitric acid solution of bismuth nitrate and a silica sol are added in order to an aqueous solution of ammonium heptamolybdate and phosphoric acid, and the composition so obtained sprayed dried and calcined to form the catalyst. This application also discloses another catalyst preparation technique in which an aqueous nitric acid solution of ferric nitrate and bismuth nitrate is added to a previously formed aqueous slurry containing ammonium heptamolybdate, phosphoric acid, arsenic acid, silica sol, nickel nitrate and cobalt nitrate, the composition so obtained heated until a gel forms, and the gel dried and calcined to produce the ultimate catalyst.

Each of the known techniques of catalyst preparation has relative advantages and disadvantages. Also, there has been some indication that the catalytic properties of the ultimate catalysts produced can be improved if specific catalysts preparation techniques are followed. As yet, however, there is no known catalyst preparation technique which is both simple and easy to perform and capable of enhancing the catalytic properties of the catalyst produced.

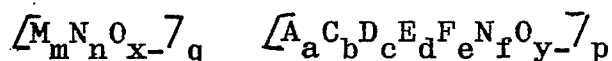
It is an object of the present invention to provide a catalyst preparation technique especially suited, but not limited to, the preparation

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of bismuth molybdate type catalysts which is both simple and easy to perform as well as capable of enhancing the catalytic properties of the catalyst produced.

According to the invention, it has been found that the catalytic activity of multi-component oxidation and ammoxidation catalysts can be significantly enhanced if the key catalytic phase (for example, bismuth molybdate in the case of a bismuth molybdate-type catalyst) is pre-formed prior to combining it with the remaining elements of the desired catalyst. This procedure not only enhances the activity of the catalyst, but is simple and easy to carry out.

The process for the preparation of catalysts according to the invention is applicable to a wide variety of different types of catalysts, the compositions of which are generally well known. Such catalysts can be described by the following general formula:



wherein: M = Bi, Te, Sb, Sn, and/or Cu
 N = Mo and/or W
 A = alkali metal, Tl, and/or Sm
 C = Ni, Co, Mn, Mg, Be, Ca, Sr, Ba, Zn, Cd, and/or Hg
 D = Fe, Cr, Ce, and/or V
 E = P, As, B, Sb
 F = rare earth, Ti, Zr, Nb, Ta, Re, Ru, Rh, Ag, Au, Al, Ga, In, Si, Ge, Pb, Th, and/or U, and further

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wherein $a = 0-4$

$b = 0-20$

$c = 0.01-20$

$d = 0-4$

5

$e = 0-8$

$f = 8-16$

$m = 0.01-10$

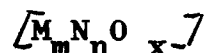
$n = 0.1-30$, and

10

x and y are numbers such that the valence requirements of the other elements for oxygen in the key catalytic phase and the host-catalyst phase, respectively are satisfied; and the ratio q/p is 0.1 to 10, preferably 0.5-4.

In such catalysts, the portion denoted by

15



is denoted as the key catalytic phase, while the portion of the catalyst defined by



20

is the host-, promotor-, and/or co-catalyst phase (hereinafter referred to as the host-catalyst phase).

25

In this connection, although the foregoing catalyst description indicates that the catalysts produced by the inventive process are composed of two phases, namely a key catalytic phase and a host-catalyst phase, this terminology is used for descriptive purposes only. Oxide catalysts of the type described are well known in the art and normally take the form of some type of oxide complex, the specific structure of which is extremely complex and not completely understood. The catalysts

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produced by the process of the invention are of a similar nature. More specifically they are not composed of a simple mixture of the key and host-catalyst phases but rather a complex composition in which the key and host-catalyst phases interact with one another and which may be composed of one or more phases.

In the foregoing formula, M is preferably Bi and N is Mo. Of these catalysts, those containing nickel, cobalt and iron and optionally phosphorous or antimony, are preferred, and of these catalysts those containing an alkali metal, most preferably potassium, rubidium and/or cesium, are especially preferred. Also, if the catalyst contains a Group IIA or IIB metal, it is preferably Mg, Cd or Zn.

An important feature of the present invention as indicated above is that the key catalytic phase of the catalyst, for example bismuth molybdate, is preformed prior to combining with the other elements of the catalyst. The key catalytic phase can be made in accordance with any conventional technique. For example, bismuth molybdate can be conveniently prepared by adding ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, to an aqueous solution of bismuth nitrate, preferably in a nitric solution, and then adjusting the pH to form a precipitate of bismuth molybdate. Alternately, other bismuth salts having decomposable anions can be employed. For example, acetate, triphenyl and citrate salts of bismuth can be

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employed to form bismuth molybdate. Similarly,
decomposable salts of the other M elements can be
used to supply the M component of the key catalytic
phase, while ammonium tungstate, tungstic acid
5 and the like can be used to supply tungsten in the
case in which N is W.

Still another technique for forming the key
catalytic phase is by known metallurgical techniques,
for example, by reacting bismuth oxide and molybdenum
10 oxide together in the solid phase.

Preparation of molybdates and/or tungstates of
the various elements M listed in the foregoing
formula are well known in the art. Thus those
skilled in the art should be able readily to produce
15 the pre-formed catalytic phase of the catalyst.

In producing the key catalytic phase of the
objective catalysts, the amount of M and N components
combined together is, of course, dependent upon the
ultimate composition of the objective catalyst as
20 well as the amount of N element in the co-catalyst
phase. Within this framework, however, it is
desirable that the ratio M/N in forming the key
catalytic phase be maintained within the range of
1:9 to 9:1, preferably 2:1 to 1:3 and most preferably
25 2:1 to 2:3. When producing bismuth molybdate as the
key catalytic phase, it is especially preferred that
the M/N ratio be 2:1 to 1:3 and most preferably 2:1
to 2:3.

The remaining elements of the desired catalyst
30 which form the host-catalyst phase can be combined

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with the preformed key catalytic phase in any manner. For example, a single solution or slurry containing all of the ingredients of the host-catalyst phase can be added to the pre-formed key catalytic phase
5 and the composition so obtained dried and calcined to produce the desired catalyst. Alternatively, one or more of the elements in the host-catalyst phase can also be pre-formed into a molybdate and/or tungstate prior to admixing with the pre-formed key
10 catalytic phase. For example, the chromium content of the host-catalyst phase can be formed into chromium molybdate (in the case of a molybdate catalyst) prior to addition to the key catalytic phase. Since, however, it is desirable that the
15 process of the invention be as simple as possible, it is preferred to form the host-catalyst phase in a single operation. In any event, it is necessary in order to keep the process of the invention simple that none of the Group VIII elements in the catalyst,
20 if any, is individually pre-formed into a molybdate or tungstate since to do so would make the preparation procedure unduly and unnecessarily complex.

As indicated above, the host-catalyst phase can be combined with the key catalytic phase in the
25 form of a solution or slurry, the solution or slurry preferably being aqueous. If a host-catalyst phase in the form of a solution is employed, the solution is added to the key catalytic phase (either in the form or a slurry) and the composition so obtained
30 heated to dryness. In accordance with well known

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chemical phenomena, heating, pH adjustment or other appropriate treatment of the aqueous composition causes precipitation of the components dissolved in the liquid phase of the slurry, thereby
5 producing a precipitate which together with the pre-formed key catalytic phase forms a pre-catalyst of appropriate composition. Drying and calcination of the pre-catalyst in accordance with conventional procedures causes decomposition of decomposable
10 anions and cations thereby yielding an activated catalyst of the desired composition.

If the host-catalyst phase is in the form of a slurry rather than a solution, this slurry is admixed with the key catalytic phase (either in the form of a
15 slurry or a solid) and the composition so obtained dried and calcined in the same manner as discussed above to produce a catalyst of the desired composition.

In a similar manner, an aqueous solution or
20 slurry containing less than all of the elements in the host-catalyst phase can be added to the key catalytic phase. In such a situation, of course, one or more additional solutions or slurries containing the remaining elements constituting the
25 host-catalyst phase must also be added to the key catalytic phase to produce the desired catalyst. In any event, the manner in which the elements of the co-catalyst phase are combined with the key catalytic phase is unimportant so long as none of
30 the Group VIII elements in the catalyst, if any, are

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preformed into molybdates and/or tungstates individually.

The starting materials used to supply particular elements for forming the host-catalyst phase can be any materials conventionally employed in the manufacture of oxidation catalysts. Normally, decomposable salts which will yield the desired elements upon heating to elevated temperatures are employed, although oxides and even free acids can be employed as can salts in which both the anion and cation contribute elements to the final catalyst such as KH_2PO_4 . For example, nitrate, acetate, triphenyl and citrate salts of the elements in question can be employed as can phosphoric acid, antimony oxide and chromium trioxide. Nitrate salts find particular applicability in prior art processes and are especially useful in the process according to the invention.

Techniques for forming oxide complex catalysts containing a wide variety of different elements and based on molybdates or tungstates are well known in the art, and those skilled in the art should have no difficulty in determining how to incorporate a particular element into the catalyst of the present invention. Provided that the key catalytic phase of the desired catalyst is pre-formed and no Group VIII element is individually preformed, the catalyst so produced will have excellent catalytic activity even though prepared by a very simple and straight forward procedure.

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In accordance with a preferred embodiment of the present invention, the desired catalyst is most simply made by combining together an aqueous slurry of the key catalytic phase and an aqueous
5 slurry of the host-catalyst phase, drying the composition so obtained to yield a solid pre-catalyst precipitate and calcining the precipitate to form a catalyst of the desired composition. The key catalytic phase aqueous slurry is preferably
10 made by co-precipitation techniques using decomposable salts (preferably nitrates and ammonium salts) and if desired, oxides and free acids and the aqueous slurry of the host-catalyst phase is similarly made by co-precipitation with decomposable
15 salts (preferably nitrates and ammonium salts) and if desired oxides and free acids.

In another very simple way of carrying out the process of the invention the starting materials used for supplying the elements of the host-catalyst
20 phase (e.g. nitrate salts, free acids, oxides, etc.) can be individually added (either in the form of a solid or a slurry) to an aqueous slurry of the key catalytic phase, and the precipitate obtained on drying calcined in the usual manner.

25 A significant feature of the process according to the invention is that the key catalytic phase of the desired catalyst once pre-formed can be combined in essentially any form with the remaining ingredients of the catalyst. For example, the key
30 catalytic phase, which is normally derived in the

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form of an aqueous slurry, can be combined with the other elements of the catalyst still in the form of this aqueous slurry. In other words, no filtering of the key catalytic phase slurry to
5 remove the mother liquor therefrom is necessary in accordance with the present invention. Indeed, filtering is undesirable since it complicates the preparation procedure. If desired, however, the pre-formed key catalytic phase can be separated
10 from the mother liquor, as by filtration, and combined with the other ingredients of the catalyst in this form. Furthermore, if desired, the key catalytic phase can be subjected to calcination with or without previous filtration in
15 a conventional manner before admixing with the other ingredients of the catalyst, although this is unnecessary. And, if calcination is carried out it is preferably accomplished under conditions insufficient to cause significant crystallization.
20 Furthermore, if the key catalytic phase is formed by techniques other than co-precipitation, such as, for example, metallurgical techniques, it can be combined with the other ingredients of the catalyst in the form derived.

25 It should also be appreciated that the order in which the various phases of the catalyst are added to one another is also not critical. More specifically, one or more components of the host-catalyst phase (either preformed or unpreformed)
30 can be added to the key catalyst phase, or

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conversely the key catalytic phase can be added to one or more of the components (either preformed or unpreformed) of the host-catalyst phase.

Furthermore, if all of the ingredients of the

5 host-catalyst phase are not simultaneously combined with the key catalytic phase, the order in which the different elements of the host-catalyst phase are combined with the key catalytic phase is also unimportant.

10 The catalysts of the present invention are calcined prior to use. As is well known in the art, calcination of oxide complex catalysts serves to activate the catalysts, i.e. increase their catalytic activity. Also, calcination serves
15 to drive off decomposable anions and cations which may be present in the pre-catalyst. In accordance with the present invention, calcination can be accomplished in the presence of oxygen, preferably air, or other gas in a conventional manner. For
20 example, the catalyst can be calcined for a period of $\frac{1}{4}$ to 48 hours at temperatures of 200 to 800°C in the presence of air.

 The catalyst of the present invention may include significant amounts of essentially inert
25 supports such as silica, alumina, alundum, pumice, titania and zirconia. Such support materials are well known in the art for supporting oxide complex type catalysts, and any conventional support material can be employed in any conventional amount.
30 When a support material is employed, it can be added

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to the remaining ingredients of the desired catalyst at any time and in any manner. For example, the support material can be added to the key catalytic phase prior to the addition of the host-catalyst phase or it can be added to the catalyst once
5 formed before or even after a calcination.

Preferably, however, the support material is added to the host-catalyst prior to combining the host-catalyst phase with the key catalytic phase.

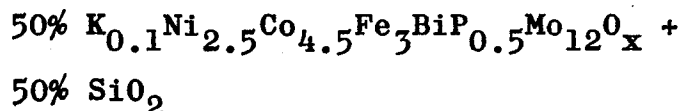
10 As indicated above, an important feature of the present invention is that the key catalytic phase of the objective catalyst is preformed prior to admixing with other ingredients of the catalyst. Although not wishing to be bound in any theory,
15 it is believed that prior art processes for making molybdate and/or tungstate catalysts were disadvantageous because the element or elements M (e.g. Bi) had to compete with the other elements in the catalyst (e.g. Ni, Co or Fe) for
20 molybdenum as the molybdate and/or tungstate species were formed. In accordance with the present invention, however, the M element is allowed to form a molybdate and/or tungstate without competition from competing elements so that the key catalytic phase can
25 properly form. As a result, the catalysts produced by the process of the present invention have superior catalytic activity compared to catalysts produced by prior art techniques.

The following Examples further explain the
30 invention:-

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Comparative Example A

A catalyst of the formula:



5 was prepared by a conventional catalyst preparation technique in the following manner:

36.36g $\text{FeNO}_3 \cdot 9\text{H}_2\text{O}$ was added to approximately 10cc H_2O and warmed by a hot plate until it dissolved/melted. Next, 14.55g $\text{BiNO}_3 \cdot 5\text{H}_2\text{O}$ was added to the solution and allowed to dissolve/melt therein. Thereafter 39.29g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added to the solution and allowed to dissolve/melt. Next 21.81g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added and allowed to dissolve/melt. Then 3.03g of 10 weight percent KNO_3 aqueous solution was added to form a dark brown solution denoted as solution A.

In a separate container, 63.56g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was dissolved in 65cc H_2O at 60°C . 205.49g of a 40 percent silica sol (Nalco) was added to the dissolved ammonium heptamolybdate. Next 3.46g of a 42 percent H_3PO_4 aqueous solution was added to form a slurry denoted as composition B.

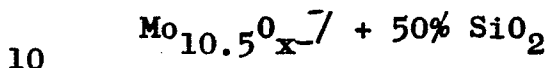
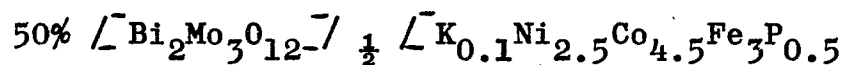
Nitrate solution A was then slowly added with stirring to composition B and as a result a light yellow slurry was formed. The slurry was heated and stirred until it thickened. The thickened material was dried at 120°C and then denitrified by heating in air at 290°C for three hours followed by heating in air at 425°C for three hours. The catalyst was then ground to a particle

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size between 0.833 mm and 0.417 mm mesh and the ground catalyst was calcined in air at 610°C for three hours to yield the desired catalyst.

Example 1

5 A catalyst having the following chemical formula was prepared by the process of the present invention:



The chemical composition of this catalyst is identical to the chemical composition of the catalyst made in Comparative Example A.

14.55g $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ was dissolved in 100 ml. of a 10 percent HNO_3 aqueous solution. 7.95g of
 15 $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was dissolved in 100 ml. H_2O with heating. The bismuth nitrate solution was then slowly added to the ammonium heptamolybdate solution with constant stirring. The pH was then adjusted to 2.5 to 3 by the addition of NH_4OH . The mixture
 20 was stirred for about one hour, thereby yielding a bismuth molybdate slurry.

In a separate container, 3.03g of a 10 percent KNO_3 aqueous solution, 21.81g $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 39.29g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 36.36g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were added
 25 to 50 ml. of water with heating. Next 55.61g $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was dissolved in 150 ml. of water with heating and to this solution was added 3.46g of a 42.5 percent aqueous solution of H_3PO_4 and 205.49g of a 40 percent silica sol (Nalco). Next, the metal
 30 nitrate solution was added to the ammonium hepta-

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molybdate/phosphoric acid solution and the mixture obtained stirred for one to two hours at 90°C to form a host-catalyst slurry.

5 The previously prepared bismuth molybdate slurry was then added to the host-catalyst slurry with stirring. The mixture obtained was evaporated to dryness with constant stirring on a hot plate and finally in a drying oven at 120°C. The dried material was then calcined in air at 290°C for three hours, 10 then 425°C for three hours, then ground and screened to a particle size between 0.833 mm and 0.417 mm mesh. The ground material was then finally calcined at 610°C for a period of three hours to yield the desired catalyst.

15 Example 2

Example 1 was repeated except that the bismuth molybdate slurry was filtered to remove the pre-formed bismuth molybdate from the mother liquor. The bismuth molybdate was then dried overnight, 20 calcined in the air at 290°C for one hour and ball milled before being added to the host-catalyst slurry.

In order to compare the catalytic properties of the catalysts produced above, a series of experiments was conducted in which propylene was 25 ammoxidized to acrylonitrile. In these experiments, 5cc of each of the above catalysts were individually charged into a plug flow microreactor and a feed comprising 1.80 propylene/2.20 NH₃/2.94 air/2.88 O₂/5.89 H₂O was fed to the reactor. The reaction 30 temperature was maintained at 430°C and the feed was

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fed to the reactor in such a way that the contact time of the reaction was 6 seconds. The results obtained are given in the following table I. In this and following tables, yield is defined as:

5

$$\% \text{ yield} = \frac{\text{moles product produced}}{\text{moles propylene fed}}$$

TABLE I

	<u>Catalyst</u>	<u>NH₃ burned</u>	<u>Acrylonitrile yield</u>	<u>HCN yield</u>
10	Comp (A)	16.4	72.7	2.8
	Ex. 1	9.0	78.0	4.6
	Ex. 2	11.9	75.8	2.8

From the foregoing table, it can be seen that the yield of the desired product, acrylonitrile, as well as useful byproduct HCN undergo a significant increase when the catalyst is produced in accordance with the inventive process. It will also be noted that the amount of NH₃ burnt is significantly reduced, which means significantly less NH₃ is wasted through the formation of NO₂. And since the amount of ammonia burnt when using molybdate and tungstate catalysts in ammoxidation reactions tends to decrease with time, even greater ammonia savings can be expected than exemplified above. These advantages as well as the fact that inventive process is simple and easy to carry out make the present invention of significant commercial importance.

In order to compare further the catalytic properties of the catalysts produced by the present

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invention with prior art catalysts, two additional experiments involving the oxidation of propylene to acrolein and acrylic acid were conducted. In these experiments, 5cc each of the catalysts of Example 1 and Comparative Example A were separately changed into a 5cc plug flow, fixed-bed reactor. A feed comprising 1 propylene/11 air/ 4H₂O was fed to the reactor in each test at a temperature of 350°C and a contact time of 3 seconds. The results obtained are set forth in the following Table II.

TABLE II			
<u>Catalyst</u>	<u>Acrolein yield</u>	<u>Acrylic acid yield</u>	<u>Sum of Acrolein & acrylic acid yields</u>
15 Comp (A)	78.3	3.8	82.1
Example 1	78.3	8.1	86.4

As can be seen, the yield of acrylic acid significantly increases when a catalyst of the present invention is used.

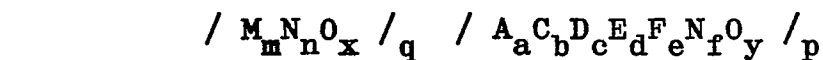
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CLAIMS:

1. A process for producing a molybdate or tungstate oxide complex catalyst wherein compounds capable of yielding the catalyst are combined together so as to form a pre-catalyst solid and the pre-catalyst solid and the pre-catalyst solid is calcined in air to activate said pre-catalyst and thereby form said catalyst, characterized in that the key catalytic phase of said catalyst comprising a molybdate and/or tungstate of Bi, Te, Sb, Sn, Cu or mixtures thereof is pre-formed prior to combining with the other elements in said catalyst; and further characterized in that none of the Group VIII elements in said catalyst, if any, is separately preformed into a molybdate or tungstate prior to combining with the key catalyst phase.

2. A process as claimed in claim 1 characterized in that the catalyst has a composition defined by the formula:



wherein M = Bi, Te, Sb, Sn and/or Cu

N = Mo and/or W

A = alkali metal, Tl, and/or Sm

C = Ni, Co, Mn, Mg, Be, Ca, Sr, Ba, Zn, Cd
and/or Hg

D = Fe, Cr, Ce, and/or V

E = P, As, B, Sb

f = rare earth, Ti, Zr, Nb, Ta, Re, Ru, Rh,
Ag, Au, Al, Ga, In, Si, Ge, Pb, Th,
and/or U, and further

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wherein a = 0-4
 b = 0-20
 c = 0.01-20
 d = 0-4
 e = 0-8
 f = 8-16
 m = 0.01-8
 n = 0.1-30, and
 x and y are numbers such that valence requirements of the other elements for oxygen in the key catalytic phase and the host-catalytic phase, respectively, are satisfied; and the ratio q/p is 0.1 to 10.

3. A process as claimed in claim 1 or claim 2 characterized in that the key catalytic phase is a bismuth molybdate.

4. A process as claimed in any of claims 1 to 3 characterized in that the key catalytic phase is made by coprecipitation to form an aqueous slurry.

5. A process as claimed in claim 4 in which the key catalytic phase is bismuth molybdate characterized in that the Bi/Mo ratio in the slurry is 9:1 to 1:9.

6. A process as claimed in claim 5 characterized in that the Bi/Mo ratio is 2:1 to 1:3.

7. A process as claimed in claim 6 characterized in that the Bi/Mo ratio is 2:1 to 2:3.

8. A process as claimed in any of claims 1 to 7 characterized in that the elements constituting said catalyst, other than the elements in said key catalytic phase, constitute a host-catalyst phase,

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which host-catalyst phase is preformed in an aqueous slurry prior to admixing with said key-catalyst phase.

9. A process as claimed in claim 8 characterized in that the pre-formed host-catalyst phase is added to the key catalytic phase in the form of a slurry without filtering said key catalytic phase slurry.

10. A process as claimed in any of claims 1 to 7 characterized in that the elements constituting said catalyst, other than elements in said key catalytic phase, constitute a host-catalyst phase and further characterized that the compounds capable of yielding the elements of said host-catalyst phase are individually added to the key catalytic phase aqueous slurry.



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EUROPEAN SEARCH REPORT

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EP 78 30 0247

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. ³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	<u>FR - A - 2 140 456</u> (KNAPSACK) * Claim 1 *	1-9	B 01 J 37/02 B 01 J 23/88 B 01 J 27/18 C 07 C 45/04 C 07 C 47/20 C 07 C 51/32 C 07 C 57/04 C 07 C 121/32 C 07 C 120/14
A	<u>FR - A - 2 148 578</u> (KNAPSACK) * Claim 1 *	1-10	
A/D	<u>US - A - 3 746 657</u> (A.F. MILLER et al.)(cited in the application) * Claim 1 *	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl. ³)
			B 01 J 37/02 B 01 J 23/88 B 01 J 27/18 B 01 J 27/02
			CATEGORY OF CITED DOCUMENTS
			X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons
			&: member of the same family, corresponding document
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 10-11-1978	Examiner ROL SAINT