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SPECIFICATION

PREPARATION OF VANADIUM ANTIMONATE
BASED CATALYSTS USING $\text{SnO}_2 \cdot x\text{H}_2\text{O}$

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a method for the preparation of tin-containing vanadium-antimony oxide catalysts useful for the catalytic ammoxidation of C_3 to C_5 paraffins or olefins, more specifically for the preparation of catalysts for the ammoxidation of propane or isobutane or propylene or isobutylene to its corresponding α, β -unsaturated mononitrile, acrylonitrile or methacrylonitrile. In addition, the catalyst may be used in the ammoxidation of methylpyridine, m-xylene or the oxidation of o-xylene to cyanopyridine, isophthalonitrile or phthalic anhydride, respectively.

More specifically, the invention relates to the use of a $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ wherein $x \geq 0$ dispersed in a solution of a tetraalkyl ammonium hydroxide as the reagent for tin in the preparation of catalysts containing vanadium and antimony and

tin in oxide form. These types of catalysts are disclosed for instance in U.S. Patent Numbers 3,681,421, 4,788,317, 5,008,427 and in British specifications 1,336,135 and 1,336,136, published in November 1973.

5 Not all sources of tin are equally effective as promoters in vanadium-antimony oxide catalysts for the oxidation and ammoxidation of saturated C_3 and C_4 alkanes, particularly ammoxidation. In fact, U.S. Patent No. 5,214,016 and EPO 691306-A1 teach that the source of tin promoter is
10 critical to the performance characteristics of the finished catalyst. It is believed that the tin should be present in very finely divided form in the precursors of such catalysts in order for the tin to be fully reactive when the solid state reaction takes place upon calcination of the catalyst
15 precursor mixture. Tin oxide sol is a suitable source in making catalysts of the present invention; see U.S. Patent No. 5,008,427. However, ground tin oxide or tin oxide made by reacting tin metal with nitric acid are decidedly less effective sources in catalyst preparation. While current
20 commercially available tin oxide sol is effective, it has a serious disadvantage because it is a very expensive source.

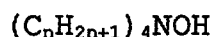
SUMMARY OF THE PRESENT INVENTION

It is an object of the present invention to provide a method of making a superior oxidation (particularly
5 ammosidation) catalyst while avoiding the use of current commercially available tin oxide sols.

It is another object of the invention to make such a catalyst at a fraction of the expense with respect to the tin component as compared to using current commercially available
10 tin oxide sol as the source of tin in the catalyst precursor.

Other objects, as well as aspects, features and advantages, of the invention will become apparent from a study of the specification including the specific examples.

The foregoing and other objects are accomplished by the
15 present invention according to which there is provided a method of making a catalyst containing vanadium, antimony and tin in the oxide state which comprises making an aqueous slurry of a mixture of source batch materials comprising compounds of the elements to be included in the final
20 catalyst, followed by drying and calcining the mixture to form an active catalyst, wherein the source batch material for the tin is a solution which comprises $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ wherein $x \geq 0$ dispersed in tetraalkyl ammonium hydroxide wherein the tetraalkyl ammonium hydroxide is defined by the following
25 formula:



wherein $5 \geq n \geq 1$.

Preferably, tetramethyl ammonium hydroxide is utilized in the practice of the invention.

5 The catalyst can be made from any suitable organic or inorganic precursor compounds of V and Sb, and compounds used to introduce other optional elements into the final catalyst after calcination, as is well known in the art, such as the salts, oxides, hydroxides or metallo-organic compounds
10 of such elements, with the tin being introduced to the batch of raw materials for preparing such catalysts in the form of a solution of $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ dispersed in tetraalkyl ammonium hydroxide as previously disclosed herein. The batch mixture of precursor materials is heated and calcined in a known
15 manner until the final catalyst results. Examples of such raw source batch materials are of course shown in the specific working examples herein.

 Particularly effective procedures for the manufacture of the catalyst are set forth in U.S. Patent Nos. 4,784,979,
20 4,879,264, 3,860,534 and 5,094,989, herein incorporated by reference. In addition, the catalyst may optionally be treated by one or more of the methods disclosed in U.S. Patent Nos. 5,432,141 and 5,498,588, also herein incorporated by reference.

25 In making the catalysts of the present invention, the upper calcining temperature is usually at least 500°C , but for

ammoxidation of paraffins this temperature is preferably over 750°C, most often at least 780°C.

The catalyst may be unsupported or supported on a suitable carrier. Preferably the catalyst is supported on a carrier such as silica, alumina, silica alumina, zirconia or mixtures thereof.

A preferred method of the invention is to make catalysts having the elements and the proportions indicated by the empirical formula:



where

A is one or more Ti, Sn, where Sn is always present

D is one or more Li, Mg, Ca, Sr, Ba, Co, Fe, Cr, Ga, Ni, Zn, Ge, Nb, Zr, Mo, W, Cu, Te, Ta, Se, Bi, Ce,

15 In, As, B, Al and Mn wherein

m is 0.5 to 10

a is greater than zero to 10

d is zero to 10

x is determined by the oxidation state of the cations present,

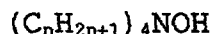
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which comprises making an aqueous slurry of a mixture of source batch materials comprising compounds of said elements to be included in the final catalyst, followed by drying and heat calcining the mixture to an active catalyst, wherein the source batch material for the tin is a solution which

25

comprises $SnO_2 \cdot xH_2O$ wherein $x \geq 0$ dispersed in tetraalkyl

ammonium hydroxide wherein the tetraalkyl ammonium hydroxide is defined by the following formula:



wherein $5 \geq n \geq 1$,

5 drying said slurry and calcining the mixture to an upper calcination temperature of at least 780°C. The upper calcination temperature can be up to 1200°C, but is most often not over 1050°C.

In another aspect of the present invention, there is
10 provided a process for making an α,β -unsaturated mononitrile selected from acrylonitrile and methacrylonitrile, by the catalytic reaction in the vapor phase of a paraffin selected from propane and isobutane with molecular oxygen and ammonia and optionally a gaseous diluent, by catalytic contact of the
15 foregoing reactants in a reaction zone with a catalyst, the feed to said reaction zone containing a mole ratio of said paraffin to NH_3 in the range from 2.5 to 16 (preferably 4 to 12; especially preferred being 5 to 11) and a mole ratio of said paraffin to O_2 in the range from 1 to 10 (preferably 2
20 to 9, especially preferred being 3 to 9), said catalyst having the empirical composition recited in the last previous paragraph, said catalyst having been made by the method of the last previous paragraph.

The catalyst may also be used in the ammoxidation of
25 methylpyridine and m-xylene to cyanopyridine and isophthalonitrile or the oxidation of o-xylene to phthalic

anhydride. The mole ratios of NH_3 to methylpyridine and O_2 to methylpyridine are 1 to 5 and 1 to 10, respectively. The mole ratios of NH_3 to m-xylene and O_2 to m-xylene are 1 to 5 and 1 to 10, respectively. In the phthalic anhydride reaction, the ratio of O_2 to o-xylene may range from 1 to 10.

The catalyst prepared by the process of the present invention may also be utilized in the ammoxidation of propylene or isobutene with ammonia and oxygen to produce acrylonitrile or methacrylonitrile. The mole ratio of NH_3 to olefin may range from about 1 to 5 and the mole ratio of O_2 to olefin may range from 1 to 10 in this reaction under conventional temperatures and conditions well known in the art.

DETAILED DESCRIPTION OF THE INVENTION

The following examples of making the catalysts and the ammoxidation reactions using the catalysts so made are exemplary only and should not be understood to be in any way limiting.

Example 1

A catalyst having the composition $\text{VSb}_{1.4}\text{Sn}_{0.2}\text{Ti}_{0.1}\text{O}_x$ (Catalyst No. 17388-79) was prepared by mixing 27.30g of V_2O_5

powder with a solution consisting of 100ml of 30% H_2O_2 in 900ml of water in a two liter beaker. After reaction of the V_2O_5 powder was complete, 61.25g of Sb_2O_3 was added followed by 2.40g of TiO_2 powder (Degussa P-25). The beaker was
5 covered with a watch glass and the mixture was stirred and heated for about 3 hours. In a separate beaker, 10.13g of $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ ("acid tin oxide" Magnesium Elektron Inc., received 6/7/91) were added to 100ml of water and 8ml of 25wt% solution of tetramethyl ammonium hydroxide. The mixture was heated on
10 a hot plate with constant stirring until a translucent mixture formed. This tin-containing dispersion was then added to the foregoing vanadium, antimony, titanium dispersion. The mixture was stirred in an uncovered beaker with heating in order to reduce the volume by evaporation of water. When the
15 mixture could no longer be stirred, it was dried in an oven at 120°C . Thereafter, it was calcined for 1 hour at 325°C then for 8 hours at 650°C , then cooled and crushed and sieved and the 20-35 mesh particles collected. A portion of this was calcined for 3 hours at 820°C then at 650°C for an additional
20 3 hours.

The calcined catalyst was then contacted with isobutanol using about 6.25ml of isobutanol per gram of catalyst by placing the catalyst in a coarse glass frit funnel, pouring the isobutanol over the catalyst, stirring the catalyst in the
25 isobutanol in order to spread the catalyst evenly over the bottom of the funnel, then allowing the isobutanol to pass

through the funnel without suction. This washing was done a total of three times. After the last of the isobutanol was passed through the funnel, the catalyst was heated in an oven at 120°C to remove the residual isobutanol on the catalyst.

5 The catalyst was evaluated for ammoxidation of propane using a 1/4" titanium U-tube fixed bed reactor. The gaseous feed to the reactor had a molar ratio of 3 propane/ 1 ammonia/ 2 oxygen/ 5 nitrogen at 15 psig pressure. At a reactor temperature of 490°C and a contact time of 1.4 seconds,
10 selectivity to acrylonitrile was 61.2% at a propane conversion of 19.2%. At a reactor temperature of 495°C and a contact time of 1.4 seconds, selectivity to acrylonitrile was 58.6% at a propane conversion of 21.2%.

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Example 2

A catalyst having the composition $\text{VSb}_{1.4}\text{Sn}_{0.2}\text{Ti}_{0.1}\text{O}_x$ was prepared by mixing 27.30g of V_2O_5 powder with a solution consisting of 100ml of 30% H_2O_2 in 900ml of water in a two
20 liter beaker. After reaction of the V_2O_5 powder was complete, 61.25g of Sb_2O_3 was added followed by 2.40g of TiO_2 powder (Degussa P-25). The beaker was covered with a watch glass and the mixture was stirred and heated for about 3 hours. In a separate beaker, 10.13g of $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ ("acid
25 tin oxide" Magnesium Elektron Inc., received 6/7/91) were added to 100ml of water and 30ml of 25wt% solution of

tetramethyl ammonium hydroxide. The mixture was heated on a hot plate with constant stirring until a translucent mixture formed. This tin-containing dispersion was then added to the foregoing vanadium, antimony, titanium dispersion. The
5 mixture was stirred in an uncovered beaker with heating in order to reduce the volume by evaporation of water. When the mixture could no longer be stirred, it was dried in an oven at 120°C. Thereafter it was calcined for 1 hour at 325°C, then for 8 hours at 650°C, then cooled and crushed and sieved and
10 the 20-35 mesh particles collected. A portion of this was calcined for 3 hours at 820°C then at 650°C for an additional 3 hours.

The calcined catalyst was then contacted with isobutanol using about 6.25ml of isobutanol per gram of catalyst by
15 placing the catalyst in a coarse glass frit funnel, pouring the isobutanol over the catalyst, stirring the catalyst in the isobutanol in order to spread the catalyst evenly over the bottom of the funnel, then allowing the isobutanol to pass through the funnel without suction. This washing was done a
20 total of three times. After the last of the isobutanol was passed through the funnel, the catalyst was heated in an oven at 120° to remove the residual isobutanol on the catalyst.

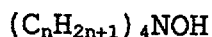
The catalyst was evaluated for ammoxidation of propane using a 1/4" titanium U-tube fixed bed reactor. The gaseous
25 feed to the reactor had a molar ratio of 3 propane/ 1 ammonia/ 2 oxygen/ 5 nitrogen at 15 psig pressure. At a reactor

temperature of 495°C and a contact time of 2.4 seconds, selectivity to acrylonitrile was 55.6% at a propane conversion of 13.1%.



What is claimed is:

1. A method of making a catalyst containing vanadium, antimony and tin in the oxide state comprising making an aqueous slurry of a mixture of source batch materials
5 comprising compounds of the elements to be included in the final catalyst, drying the mixture, and calcining the mixture to form an active catalyst, wherein the source batch material for the tin is a solution which comprises $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ wherein $x \geq 0$ dispersed in tetraalkyl ammonium hydroxide wherein the
10 tetraalkyl ammonium hydroxide is defined by the following formula:



wherein $5 \geq n \geq 1$.

2. The method of claim 1 wherein the $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ is
15 dispersed in tetramethyl ammonium hydroxide.

3. The process of claim 1 wherein the calcination is at a temperature of at least 500°C .

4. The process of claim 3 wherein the calcination ammoxidation of paraffins this temperature is at least 750°C .

- 20 5. The process of claim 3 wherein the calcination temperature is at least 780°C .

6. The method of claim 1 wherein the catalyst is supported on an inert carrier.

7. The method of claim 6 wherein the carrier is
25 selected from the group consisting of silica, alumina, silica alumina, zirconia or mixtures thereof.



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8. A method of preparing a catalyst having the elements and the proportions indicated by the following empirical formula:



5 where

A is one or more Ti, Sn, where Sn is always present

D is one or more Li, Mg, Ca, Sr, Ba, Co, Fe, Cr, Ga, Ni, Zn, Ge, Nb, Zr, Mo, W, Cu, Te, Ta, Se, Bi, Ce, In, As, B, Al and Mn wherein

10 m is 0.5 to 10

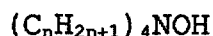
a is greater than zero to 10

d is zero to 10

x is determined by the oxidation state of the cations present,

15 comprising making an aqueous slurry of a mixture of source batch materials comprising compounds of said elements to be included in the final catalyst, followed by drying and heat calcining the mixture to an active catalyst, wherein the source batch material for the tin is a solution which

20 comprises $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ wherein $x \geq 0$ dispersed in tetraalkyl ammonium hydroxide wherein the tetraalkyl ammonium hydroxide is defined by the following formula:



wherein $5 \geq n \geq 1$,

25 drying said slurry and calcining the mixture to an upper calcination temperature of at least 500°C.



9. The method of claim 8 wherein the calcination temperature is at least 750°C.

10. The method of claim 9 wherein the calcination temperature is at least 780°C.

5 11. The method of claim 8 wherein the catalyst is supported on an inert carrier.

12. The method of claim 11 wherein the inert carrier is selected from the group consisting of silica, alumina, zirconia, silica alumina or mixtures thereof.

10 13. The method of claim 8 wherein the $\text{SnO}_2 \cdot x\text{H}_2\text{O}$ is dispersed in tetramethyl ammonium hydroxide.

14. A process for making an α, β -unsaturated mononitrile selected from acrylonitrile and methacrylonitrile, by the catalytic reaction in the vapor phase of a paraffin selected
15 from propane and isobutane with molecular oxygen and ammonia by catalytic contact of the foregoing reactants in a reaction zone with a catalyst having the following formula



where

20 A is one or more Ti, Sn, where Sn is always present

D is one or more Li, Mg, Ca, Sr, Ba, Co, Fe, Cr, Ga, Ni, Zn, Ge, Nb, Zr, Mo, W, Cu, Te, Ta, Se, Bi, Ce, In, As, B, Al and Mn wherein

m is 0.5 to 10

25 a is greater than zero to 10

d is zero to 10



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x is determined by the oxidation state of the cations present,

the feed to said reaction zone containing a mole ratio of said paraffin to NH_3 in the range from 2.5 to 16 and a mole ratio
5 of said paraffin to O_2 in the range from 1 to 10, wherein the catalyst has been prepared by the method of claim 1.

15. A process for making an α, β -unsaturated mononitrile selected from acrylonitrile and methacrylonitrile, by the catalytic reaction in the vapor phase of a paraffin selected
10 from propane and isobutane with molecular oxygen and ammonia by catalytic contact of the foregoing reactants in a reaction zone with a catalyst having the following formula



where

15 A is one or more Ti, Sn, where Sn is always present
D is one or more Li, Mg, Ca, Sr, Ba, Co, Fe, Cr, Ga, Ni, Zn, Ge, Nb, Zr, Mo, W, Cu, Te, Ta, Se, Bi, Ce, In, As, B, Al and Mn wherein
m is 0.5 to 10
20 a is greater than zero to 10
d is zero to 10
x is determined by the oxidation state of the cations present,

the feed to said reaction zone containing a mole ratio of said
25 paraffin to NH_3 in the range from 2.5 to 16 and a mole ratio



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of said paraffin to O_2 in the range from 1 to 10, wherein the catalyst has been prepared by the method of claim 8.

16. A process for making a compound selected from the group consisting of cyanopyridine and isophthalonitrile by the catalytic reaction in the vapor phase of a starting material selected from the group consisting of methylpyridine and m-xylene with molecular oxygen and ammonia by catalytic contact of the foregoing reactants in a reaction zone with a catalyst having the following formula



where

A is one or more Ti, Sn, where Sn is always present

D is one or more Li, Mg, Ca, Sr, Ba, Co, Fe, Cr, Ga, Ni, Zn, Ge, Nb, Zr, Mo, W, Cu, Te, Ta, Se, Bi, Ce, In, As, B, Al and Mn wherein

m is 0.5 to 10

a is greater than zero to 10

d is zero to 10

x is determined by the oxidation state of the cations present,

the feed to said reaction zone containing a mole ratio of NH_3 to starting material in the range from 1 to 5 and a mole ratio of said O_2 to said starting material in the range from 1 to 10, wherein the catalyst has been prepared by the method of claim 1.



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17. A process for making phthalic anhydride from o-xylene by the catalytic reaction in the vapor phase of o-xylene with molecular oxygen by catalytic contact of the foregoing reactants in a reaction zone with a catalyst having
5 the following formula



where

A is one or more Ti, Sn, where Sn is always present

10 D is one or more Li, Mg, Ca, Sr, Ba, Co, Fe, Cr, Ga,
Ni, Zn, Ge, Nb, Zr, Mo, W, Cu, Te, Ta, Se, Bi, Ce,
In, As, B, Al and Mn wherein

m is 0.5 to 10

a is greater than zero to 10

d is zero to 10

15 x is determined by the oxidation state of the cations
present,

the feed to said reaction zone containing a mole ratio of said O_2 to o-xylene in the range from 1 to 10, wherein the catalyst has been prepared by the method of claim 1.

20 18. A process for making an α, β -unsaturated mononitrile selected from acrylonitrile and methacrylonitrile by the catalytic reaction in the vapor phase of an olefin selected from propylene and isobutene with ammonia, and an oxygen containing gas by catalytic contact of the foregoing reactants
25 in a reaction zone with a catalyst having the following formula



where

A is one or more Ti, Sn, where Sn is always present

D is one or more Li, Mg, Ca, Sr, Ba, Co, Fe, Cr, Ga,

5 Ni, Zn, Ge, Nb, Zr, Mo, W, Cu, Te, Ta, Se, Bi, Ce,

In, As, B, Al and Mn wherein

m is 0.5 to 10

a is greater than zero to 10

d is zero to 10

10 x is determined by the oxidation state of the cations
present,

the feed to said reaction zone containing a mole ratio of
ammonia to said olefin in the range of 1 to 5 and a mole ratio
of oxygen to said olefin in the range from 1 to 10 wherein the
15 catalyst has been prepared by the method of claim 1.