

PROCESS FOR THE AMMOXIDATION OR OXIDATION OF PROPANE AND ISOBUTANE

BACKGROUND OF THE INVENTION

5 The present invention generally relates to a process for the ammoxidation or oxidation of a saturated or unsaturated hydrocarbon to produce an unsaturated nitrile or an unsaturated organic acid. The invention particularly relates to a process for the gas-phase conversion of propane to acrylonitrile and isobutane to methacrylonitrile (via ammoxidation) or of propane to acrylic acid and isobutane to methacrylic acid (via
10 oxidation).

Description of the Prior Art

Mixed metal oxide catalysts have been employed for the conversion of propane to acrylonitrile and isobutane to methacrylonitrile (via an ammoxidation reaction) and/or for conversion of propane to acrylic acid (via an oxidation reaction). The art known in
15 this field includes numerous patents and patent applications, including for example, U.S. Patent No. 5,750,760 to Ushikubo et al., U.S. Patent No. 6,036,880 to Komada et al., U.S. Patent No. 6,043,186 to Komada et al., U.S. Patent No. 6,143,916 to Hinago et al., U.S. Patent No. 6,514,902 to Inoue et al., U.S. Patent Application No. US 2003/0088118 A1 by Komada et al., U.S. Patent Application No. 2004/0063990 A1 to Gaffney et al.,
20 and PCT Patent Application No. WO 2004/108278 A1 by Asahi Kasei Kabushiki Kaisha.

Oxide promoters such as niobium, tellurium, and antimony oxides have been introduced into mixed metal oxide catalysts for propane oxidation containing Mo-V-O by incipient impregnation of metal isopropoxide solutions. The impregnated catalysts
25 were then dried and calcined.

Mixed metal oxide catalysts have been surface-modified by vapor deposition of tellurium and improved catalyst performance was reported. Further improvement was seen when a post-modification treatment with oxygen was performed.

A tellurium compound and optionally a molybdenum compound have been added
30 as catalyst activators to a compound oxide catalyst containing molybdenum, tellurium, vanadium, and niobium. The catalyst activator is added to the reactor after some time on-stream in order to maintain catalyst activity.

A tellurium compound and/or a molybdenum compound have been added as a compensative compound to a used catalyst containing molybdenum, vanadium, niobium,
35 and antimony. More generally, it has been known to add a molybdenum compound to a

reactor employing a catalyst containing molybdenum.

Although advancements have been made in the art in connection with catalysts containing molybdenum, vanadium, antimony and other components effective for conversion of propane to acrylonitrile and isobutane to methacrylonitrile (via an ammoxidation reaction) and/or for conversion to acrylic acid and isobutane to methacrylic acid (via an oxidation reaction) the catalysts need further improvement before becoming commercially viable. In general, the art-known catalytic systems for such reactions suffer from generally low yields of the desired product.

Processes that produce higher yield of useful product would be desirable. Also desirable would be catalysts that have improved stability under reaction conditions and/or improved resistance to temperature fluctuations in the reactor.

SUMMARY OF THE INVENTION

In one embodiment, the invention provides a process for the ammoxidation or oxidation of a saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon to produce an unsaturated nitrile or an unsaturated organic acid, said process comprising: providing a catalyst mixture comprising a fresh mixed metal oxide catalyst comprising molybdenum, vanadium, niobium, and at least one element selected from the group consisting of antimony and tellurium, a used mixed metal oxide catalyst comprising molybdenum, vanadium, niobium, and at least one element selected from the group consisting of antimony and tellurium, and a performance modifier selected from the group consisting of aluminum compounds, antimony compounds, arsenic compounds, boron compounds, cerium compounds, germanium compounds, lithium compounds, molybdenum compounds, neodymium compounds, niobium compounds, phosphorus compounds, selenium compounds, tantalum compounds, tellurium compounds, titanium compounds, tungsten compounds, vanadium compounds, zirconium compounds, and mixtures thereof; and contacting the saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon with an oxygen-containing gas, or with an oxygen-containing gas and ammonia, in the presence of the catalyst mixture. In certain embodiments, the catalyst mixture includes two or more performance modifier compounds.

The present invention also includes a process for the ammoxidation of a saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon to produce an unsaturated nitrile, said process comprising providing a catalyst mixture comprising a performance modifier selected from the group consisting of aluminum compounds, antimony compounds, arsenic compounds, boron compounds, cerium compounds,

germanium compounds, lithium compounds, neodymium compounds, niobium compounds, phosphorus compounds, selenium compounds, tantalum compounds, tellurium compounds, titanium compounds, tungsten compounds, vanadium compounds, zirconium compounds, and mixtures thereof; a fresh mixed metal oxide catalyst; and a
 5 used mixed metal oxide catalyst; wherein said fresh and said used catalyst are each independently defined by the empirical formula:



wherein X is selected from the group consisting of W, Te, Ti, Sn, Ge, Zr, Hf, Li, and mixtures thereof; L is selected from the group consisting of Ce, La, Pr, Nd, Sm, Eu,
 10 Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and mixtures thereof; $0.1 \leq a \leq 1.0$, $0.01 \leq b \leq 1.0$, $0.001 \leq c \leq 0.25$, $0 \leq d \leq 0.6$, $0 \leq e \leq 1$; n is the number of oxygen atoms required to satisfy valance requirements of all other elements present in the mixed oxide with the proviso that one or more of the other elements in the mixed oxide can be present in an oxidation state lower than its highest oxidation state, a, b, c, d and e represent the molar
 15 ratio of the corresponding element to one mole of Mo; and contacting the saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon with ammonia and an oxygen-containing gas in the presence of the catalyst mixture.

In one embodiment, the invention provides a process for the ammoxidation or oxidation of a saturated or unsaturated or mixture of saturated and unsaturated
 20 hydrocarbon to produce an unsaturated nitrile or an unsaturated organic acid, said process comprising: providing a catalyst mixture comprising a physical mixture of a mixed metal oxide catalyst and a performance modifier, wherein the mixed metal oxide catalyst comprises molybdenum, vanadium, niobium, and at least one element selected from the group consisting of antimony and tellurium, and wherein the performance
 25 modifier is selected from the group consisting of aluminum compounds, antimony compounds, arsenic compounds, boron compounds, cerium compounds, germanium compounds, lithium compounds, neodymium compounds, niobium compounds, phosphorus compounds, selenium compounds, tantalum compounds, tellurium compounds, titanium compounds, tungsten compounds, vanadium compounds, zirconium compounds, and mixtures thereof; and contacting the saturated or unsaturated
 30 or mixture of saturated and unsaturated hydrocarbon with an oxygen-containing gas, or with an oxygen-containing gas and ammonia, in the presence of the catalyst mixture.

The present invention also includes a process for the ammoxidation or oxidation of a saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon to
 35 produce an unsaturated nitrile or an unsaturated organic acid, said process comprising:

combining a catalyst composition and a performance modifier to form a catalyst mixture, wherein the catalyst composition comprises a mixed oxide defined by the empirical formula:



- 5 wherein X is selected from the group consisting of W, Te, Ti, Sn, Ge, Zr, Hf, Li, and mixtures thereof; L is selected from the group consisting of Ce, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and mixtures thereof; $0.1 \leq a \leq 1.0$, $0.01 \leq b \leq 1.0$, $0.001 \leq c \leq 0.25$, $0 \leq d \leq 0.6$, $0 \leq e \leq 1$; n is the number of oxygen atoms required to satisfy valance requirements of all other elements present in the mixed oxide with the
- 10 proviso that one or more of the other elements in the mixed oxide can be present in an oxidation state lower than its highest oxidation state, a, b, c, d and e represent the molar ratio of the corresponding element to one mole of Mo, and wherein the performance modifier is selected from the group consisting of aluminum compounds, antimony compounds, arsenic compounds, boron compounds, cerium compounds, germanium
- 15 compounds, lithium compounds, neodymium compounds, niobium compounds, phosphorus compounds, selenium compounds, tantalum compounds, tellurium compounds, titanium compounds, tungsten compounds, vanadium compounds, zirconium compounds, and mixtures thereof; and contacting the saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon with an oxygen-containing gas, or
- 20 with an oxygen-containing gas and ammonia, in the presence of the catalyst mixture.

- In one embodiment, the present invention relates to a process for the ammoxidation of a saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon to produce an unsaturated nitrile, said process comprising: combining a catalyst composition and a performance modifier to form a catalyst mixture, wherein the
- 25 catalyst composition comprises a mixed oxide defined by the empirical formula:



- wherein X is selected from the group consisting of W, Te, Ti, Sn, Ge, Zr, Hf, Li, and mixtures thereof; L is selected from the group consisting of Ce, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and mixtures thereof; $0.1 \leq a \leq 1.0$, $0.01 \leq b \leq 1.0$,
- 30 $0.001 \leq c \leq 0.25$, $0 \leq d \leq 0.6$, $0 \leq e \leq 1$; n is the number of oxygen atoms required to satisfy valance requirements of all other elements present in the mixed oxide with the proviso that one or more of the other elements in the mixed oxide can be present in an oxidation state lower than its highest oxidation state, a, b, c, d and e represent the molar ratio of the corresponding element to one mole of Mo, and wherein the performance
- 35 modifier is selected from the group consisting of aluminum compounds, antimony

compounds, arsenic compounds, boron compounds, cerium compounds, germanium compounds, lithium compounds, neodymium compounds, niobium compounds, phosphorus compounds, selenium compounds, tantalum compounds, tellurium compounds, titanium compounds, tungsten compounds, vanadium compounds, zirconium compounds, and mixtures thereof; and contacting the saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon with ammonia and an oxygen-containing gas in the presence of the catalyst mixture.

DETAILED DESCRIPTION OF THE INVENTION

The present invention generally relates to a process for the (amm)oxidation of a saturated or unsaturated hydrocarbon, and catalyst compositions that may be used in the process. Such processes are effective for the ammoxidation of propane to acrylonitrile and isobutane to methacrylonitrile and/or for the conversion of propane to acrylic acid and isobutane to methacrylic acid (via an oxidation reaction).

In one or more embodiments, unsaturated nitrile is prepared by a process including the ammoxidation of a saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon, and includes the steps of combining a performance modifier, a fresh mixed oxide catalyst composition, and a used mixed oxide catalyst composition to form a catalyst mixture, and contacting the hydrocarbon with ammonia and an oxygen-containing gas in the presence of the catalyst mixture.

The present invention provides a process for the ammoxidation or oxidation of a saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon to produce an unsaturated nitrile or an unsaturated organic acid, said process comprising: providing a catalyst mixture comprising a fresh mixed metal oxide catalyst comprising molybdenum, vanadium, niobium, and at least one element selected from the group consisting of antimony and tellurium, a used mixed metal oxide catalyst comprising molybdenum, vanadium, niobium, and at least one element selected from the group consisting of antimony and tellurium, and a performance modifier selected from the group consisting of aluminum compounds, antimony compounds, arsenic compounds, boron compounds, cerium compounds, germanium compounds, lithium compounds, neodymium compounds, niobium compounds, phosphorus compounds, selenium compounds, tantalum compounds, tellurium compounds, titanium compounds, tungsten compounds, vanadium compounds, zirconium compounds, and mixtures thereof; and contacting the saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon with an oxygen-containing gas, or with an oxygen-containing gas and ammonia, in the presence of the catalyst mixture.

As an embodiment, the catalyst modifier is selected from the group consisting of aluminum nitrate, alumina, antimony(III) oxide, antimony(III) oxalate, antimony (III) tartrate, antimony(V) oxide, antimony tetroxide, Sb_6O_{13} , arsenic(III) oxide, arsenic(V) oxide, arsenic acid, boron oxide, boric acid, ceric ammonium nitrate, cerium acetate, cerium(III) oxalate hydrate, cerium(IV) oxide, germanium(IV) oxide, lithium oxide, lithium hydroxide, lithium acetate, lithium nitrate, lithium tartrate, ammonium niobium oxalate, niobium oxalate niobium oxide, phosphorus pentoxide, ammonium phosphate, selenium dioxide, tantalum(V) oxide, telluric acid, tellurium dioxide, tellurium trioxide, rutile titanium dioxide (TiO_2), anatase titanium dioxide (TiO_2), titanium isopropoxide, TiO(oxalate), tungsten trioxide, vanadyl oxalate, vanadium (III) oxide, vanadium (IV) oxide, vanadium(V) oxide, zirconyl nitrate, zirconia, and mixtures thereof.

Further as an embodiment, the catalyst mixture comprises at least about 0.01 moles of performance modifier per mole of Mo in the total amount of fresh and used mixed metal oxide catalyst. In another embodiment, the present invention comprises combining a fresh mixed oxide catalyst and a performance modifier via wet impregnation. As an aspect of the present invention one or both of the fresh mixed oxide catalyst and the used mixed oxide catalyst are prepared by using a non-hydrothermal synthesis method. Further, the present invention can comprise physically mixing the fresh mixed oxide catalyst, the used fresh mixed oxide catalyst, and the performance modifier; wherein said step of providing further comprises the step of pre-mixing the fresh mixed oxide catalyst composition and the performance modifier. Moreover, the present invention can comprise the step of heating or calcining said catalyst mixture.

In an embodiment, the fresh catalyst composition comprises a mixed oxide defined by the empirical formula:



wherein X is selected from the group consisting of W, Te, Ti, Sn, Ge, Zr, Hf, Li, and mixtures thereof; L is selected from the group consisting of Ce, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and mixtures thereof; $0.1 \leq a \leq 1.0$, $0.01 \leq b \leq 1.0$, $0.001 \leq c \leq 0.25$, $0 \leq d \leq 0.6$, $0 \leq e \leq 1$; n is the number of oxygen atoms required to satisfy valance requirements of all other elements present in the mixed oxide with the proviso that one or more of the other elements in the mixed oxide can be present in an oxidation state lower than its highest oxidation state, a, b, c, d, and e represent the molar ratio of the corresponding element to one mole of Mo.

In an embodiment, the used catalyst composition comprises a mixed oxide defined by the empirical formula:



wherein X is selected from the group consisting of W, Te, Ti, Sn, Ge, Zr, Hf, Li, and mixtures thereof; L is selected from the group consisting of Ce, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and mixtures thereof; $0.1 \leq a \leq 1.0$, $0.01 \leq b \leq 1.0$, $0.001 \leq c \leq 0.25$, $0 \leq d \leq 0.6$, $0 \leq e \leq 1$; n is the number of oxygen atoms required to satisfy valance requirements of all other elements present in the mixed oxide with the proviso that one or more of the other elements in the mixed oxide can be present in an oxidation state lower than its highest oxidation state, a, b, c, d, and e represent the molar ratio of the corresponding element to one mole of Mo.

The present invention also provides a process for the ammoxidation or oxidation of a saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon to produce an unsaturated nitrile or an unsaturated organic acid, said process comprising: physically mixing a dry mixed metal oxide catalyst and a performance modifier to form a catalyst mixture, wherein the mixed metal oxide catalyst comprises molybdenum, vanadium, niobium, and at least one element selected from the group consisting of antimony and tellurium, and wherein the performance modifier is selected from the group consisting of aluminum compounds, antimony compounds, arsenic compounds, boron compounds, cerium compounds, germanium compounds, lithium compounds, neodymium compounds, niobium compounds, phosphorus compounds, selenium compounds, tantalum compounds, titanium compounds, tungsten compounds, vanadium compounds, zirconium compounds, and mixtures thereof; and contacting the saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon with an oxygen-containing gas, or with an oxygen-containing gas and ammonia, in the presence of the catalyst mixture.

The performance modifier, of the invention, is selected from the group consisting of aluminum nitrate, alumina, antimony(III) oxide, antimony(III) oxalate, antimony (III) tartrate, antimony(V) oxide, antimony tetroxide, Sb_6O_{13} , arsenic(III) oxide, arsenic(V) oxide, arsenic acid, boron oxide, boric acid, ceric ammonium nitrate, cerium acetate, cerium(III) oxalate hydrate, cerium(IV) oxide, germanium(IV) oxide, lithium oxide, lithium hydroxide, lithium acetate, lithium nitrate, lithium tartrate, neodymium (III) chloride, neodymium (III) oxide, neodymium (III) isopropoxide, neodymium (III) acetate hydrate, ammonium niobium oxalate, niobium oxalate niobium oxide, phosphorus pentoxide, ammonium phosphate, selenium dioxide, tantalum(V) oxide, rutile titanium dioxide (TiO_2), anatase titanium dioxide (TiO_2), titanium isopropoxide, $\text{TiO}(\text{oxalate})$, tungsten trioxide, vanadyl oxalate, vanadium (III) oxide, vanadium (IV)

oxide, vanadium(V) oxide, zirconyl nitrate, zirconia, and mixtures thereof.

As an embodiment, the mixed metal oxide catalyst further comprises at least one element selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, tungsten, titanium, tin, germanium, zirconium, lithium, and hafnium. One or more of the mixed metal oxide catalyst and the performance modifier comprises a support selected from the group consisting of silica, alumina, zirconia, titania, or mixtures thereof. Also, the catalyst mixture can comprise at least about 0.01 moles of performance modifier per mole of Mo in the mixed metal oxide catalyst. In an aspect of the invention, the step of physically mixing comprises mixing a calcined mixed metal oxide catalyst and a performance modifier.

In an embodiment, the mixed metal oxide catalyst comprises a mixed oxide defined by the empirical formula:



wherein X is selected from the group consisting of W, Te, Ti, Sn, Ge, Zr, Hf, Li, and mixtures thereof; L is selected from the group consisting of Ce, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and mixtures thereof; $0.1 \leq a \leq 1.0$, $0.01 \leq b \leq 1.0$, $0.001 \leq c \leq 0.25$, $0 \leq d \leq 0.6$, $0 \leq e \leq 1$; n is the number of oxygen atoms required to satisfy valance requirements of all other elements present in the mixed oxide with the proviso that one or more of the other elements in the mixed oxide can be present in an oxidation state lower than its highest oxidation state, a, b, c, d, and e represent the molar ratio of the corresponding element to one mole of Mo.

As an embodiment, the ammoxidation of a saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon, wherein said step of contacting comprises contacting the saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon with ammonia and an oxygen-containing gas in the presence of the catalyst mixture.

An aspect of the invention provides that the dry mixed metal oxide catalyst is prepared by a non-hydrothermal synthesis method.

Additionally, an embodiment of the invention provides a step of physically mixing comprises mixing an un-calcined or partially calcined dry mixed metal oxide catalyst and a performance modifier to form a mixture, and further comprises the step of calcining the mixture.

Performance Modifier

The performance modifier may be mixed with the catalyst prior to introducing the catalyst into a reactor. In one or more embodiments, the performance modifier is a compound or a mixture of compounds selected from the group consisting of aluminum compounds, antimony compounds, arsenic compounds, boron compounds, cerium compounds, germanium compounds, lithium compounds, molybdenum compounds, neodymium compounds, niobium compounds, phosphorus compounds, selenium compounds, tantalum compounds, tellurium compounds, titanium compounds, tungsten compounds, vanadium compounds, and zirconium compounds. In one or more
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embodiments, the performance modifier may be supported on an inert support including but not limited to silica, titania, zirconia or mixtures thereof.

Examples of aluminum compounds include aluminum nitrate and alumina (Al_2O_3). Examples of antimony compounds include antimony oxides, antimony oxalates, and antimony tartarates. Specific examples include antimony(III) oxide, antimony(III) oxalate, antimony (III) tartarate, and antimony(V) oxide, antimony tetroxide (Sb_2O_4), and Sb_6O_{13} . Examples of arsenic compounds include arsenic(III) oxide, arsenic(V) oxide, and arsenic acid. Examples of boron compounds include boron oxide, and boric acid.

Examples of cerium compounds include ceric ammonium nitrate, cerium acetate, cerium(III) oxalate hydrate, and cerium(IV) oxide. Examples of germanium compounds include germanium(IV) oxide. Examples of lithium compounds include lithium hydroxide, lithium oxide, lithium nitrate, lithium acetate, and lithium tartrate.

Examples of molybdenum compounds include molybdenum (VI) oxide (MoO_3), ammonium heptamolybdate and molybdic acid. Examples of neodymium compounds include neodymium (III) chloride, neodymium (III) oxide, neodymium (III) isopropoxide, and neodymium (III) acetate hydrate. Examples of niobium compounds include ammonium niobium oxalate, niobium oxalate and niobium oxide.

Examples of phosphorus compounds include phosphorus pentoxide and ammonium phosphate. Examples of selenium compounds include selenium dioxide. Examples of tantalum compounds include tantalum(V) oxide. Examples of tellurium
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compounds include telluric acid, tellurium dioxide, and tellurium trioxide.

Examples of titanium compounds include rutile and/or anatase titanium dioxide (TiO_2), titanium isopropoxide, and $\text{TiO}(\text{oxalate})$. Titanium dioxide is available as Degussa P-25, Tronox A-K-1, and Tronox 8602 (formerly named A-K-350). Examples of tungsten compounds include tungsten trioxide, tungstic acid, and ammonium tungstate. Examples of vanadium compounds include vanadyl oxalate, vanadium (III)

oxide, vanadium (IV) oxide, ammonium metavanadate, and vanadium(V) oxide. Examples of zirconium compounds include zirconyl nitrate and zirconia (ZrO_2).

In one or more embodiments, two or more performance modifier compounds are employed. The modifier compounds may be added to the catalyst mixture
5 simultaneously or sequentially. The modifier compounds may be pre-mixed or added to the catalyst mixture individually.

In one embodiment, the performance modifier is a solid that may be physically mixed with a mixed oxide catalyst to improve catalyst performance. The performance modifier may be heat treated or mechanically treated, including for example by grinding,
10 sieving and/or pressing, prior to use in the process of the present invention.

In other embodiments, the performance modifier may be incorporated into a solution or slurry that may be used to impregnate a mixed oxide catalyst composition with the performance modifier.

The amount of performance modifier that is added to the catalyst mixture is not
15 particularly limited. In one embodiment, the amount of performance modifier may be expressed in terms of moles of the performance modifier per mole of molybdenum in the total amount of fresh and used mixed oxide catalyst. In one or more embodiments, the catalyst mixture comprises at least about 0.01 moles performance modifier per mole of molybdenum. In these or other embodiments, the catalyst mixture comprises up to about
20 1.0 moles performance modifier per mole of molybdenum in the total amount of fresh and used mixed oxide catalyst. In one embodiment, the catalyst mixture comprises from about 0.01 to about 1.0 moles performance modifier per mole of molybdenum. In another embodiment, the catalyst mixture comprises from about 0.011 to about 0.5, and in yet another embodiment, from about 0.012 to about 0.2 moles performance modifier
25 per mole of molybdenum in the total amount of fresh and used mixed oxide catalyst.

Also, performance modifier further comprises a molybdenum compound. The performance modifier can comprise antimony (III) oxide, antimony(III) oxalate, antimony (III) tartrate, antimony(V) oxide, antimony tetroxide, Sb_6O_{13} , germanium (IV) oxide, telluric acid, lithium hydroxide, or cerium (IV) oxide or a mixture thereof.

30 In an embodiment, the performance modifier comprises antimony (III) oxide, antimony(III) oxalate, antimony (III) tartrate, antimony(V) oxide, antimony tetroxide, Sb_6O_{13} , or a mixture thereof. Also, the performance modifier can further comprise a tellurium compound.

As an embodiment, one or more of the performance modifier, the fresh mixed
35 metal oxide catalyst, and the used mixed metal oxide catalyst comprises a support

selected from the group consisting of silica, alumina, zirconia, titania, or mixtures thereof.

Mixed Oxide Catalyst Composition

The improved process of the present invention has application for a number of fresh and used mixed oxide ammoxidation and oxidation catalyst compositions. As used herein, the term fresh catalyst refers to catalyst that has not been exposed to a reactor feedstream. As used herein, the term used catalyst refers to catalyst that has been exposed to a reactor feedstream. In certain embodiments, the fresh and used catalysts have the same initial composition, and in other embodiments, the initial compositions of the fresh and used catalysts are different. The description hereinbelow of the mixed oxide catalyst composition and the preparation thereof applies to both the fresh and used catalyst compositions of the present invention.

In one embodiment, the mixed oxide catalyst composition comprises molybdenum, vanadium, niobium, and one or both of antimony and tellurium. In one or more embodiments, the mixed oxide catalyst further includes at least one element selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. In certain embodiments, the catalyst composition may include at least one element selected from the group consisting of tungsten, tellurium, titanium, tin, germanium, zirconium, and hafnium. As used herein, "at least one element selected from the group ..." or "at least one lanthanide selected from the group ..." includes within its scope mixtures of two or more of the listed elements or lanthanides, respectively.

In one embodiment, one or both of the fresh and used mixed oxide catalysts comprise molybdenum, vanadium, antimony and niobium, and may be independently defined by the empirical formula:



wherein X is selected from the group consisting of W, Te, Ti, Sn, Ge, Zr, Hf, Li, and mixtures thereof,

L is selected from the group consisting of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and mixtures thereof,

$$0.1 \leq a \leq 1.0,$$

$$0.01 \leq b \leq 1.0,$$

$$0.001 \leq c \leq 0.25,$$

$$0 \leq d \leq 0.6,$$

$$0 \leq e \leq 1; \text{ and}$$

n is number of oxygen atoms required to satisfy valance requirements of all other elements present in the mixed oxide with the proviso that one or more of the other elements in the mixed oxide can be present in an oxidation state lower than its highest oxidation state, and a, b, c, d, and e represent the molar ratio of the corresponding element to one mole of Mo.

In one or more embodiments, where the catalyst compositions are employed in an ammoxidation process, X may be selected from the group consisting of W, Te, Ti, Ge, Sn, Zr, Hf, Li, and mixtures thereof. In other embodiments, X may be selected from the group consisting of W, Te, Ti, Sn, Zr, Hf, Li, and mixtures thereof. In other
10 embodiments of the catalyst compositions described by the above empirical formulas X is one of W, Te, Ti, Li, or Sn. In other embodiments of the catalyst compositions described by the above empirical formulas X is W.

In one or more embodiments, where the catalyst compositions are employed in an ammoxidation process, L may be selected from the group consisting of La, Ce, Pr, Nd,
15 Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. In other embodiments of the catalyst compositions described by the above empirical formulas, L is Pr, L is Nd, L is Sm, L is Eu, L is Gd, L is Tb, L is Dy, L is Ho, L is Er, L is Tm, L is Yb, and L is Lu. In other embodiments of the catalyst compositions described by the above empirical formulas, L is one of Nd, Ce or Pr.

In other embodiments of the catalyst compositions described by the above empirical formulas, a, b, c, and d are each independently within the following ranges: $0.1 \leq a$, $0.2 < a$, $a < 0.3$, $a < 0.4$, $a < 0.8$, $a \leq 1.0$, $0.01 \leq b$, $0.05 < b$, $0.1 < b$, $b < 0.3$, $b < 0.6$, $b \leq 1.0$, $0.001 \leq c$, $0.01 < c$, $0.02 < c$, $0.03 < c$, $0.04 < c$, $c < 0.05$, $c < 0.1$, $c < 0.15$, $c < 0.2$, $c \leq 0.25$, $0 \leq d$, $0.001 < d$, $0.002 < d$, $0.003 < d$, $0.004 < d$, $d < 0.006$, $d < 0.01$, $d < 0.02$, $d < 0.05$, $d < 0.1$, $d \leq 0.2$, $0 \leq e$, $0.001 < e$, $e < 0.006$, $e < 0.01$, $e < 0.02$, $e < 0.04$, $e < 0.1$, $e \leq 1$.

The catalyst of the present invention may be made either supported or unsupported (i.e. the catalyst may comprise a support or may be a bulk catalyst). Suitable supports are silica, alumina, zirconia, titania, or mixtures thereof. However,
30 when zirconia or titania are used as support materials then the ratio of molybdenum to zirconium or titanium increases over the values shown in the above formulas, such that the Mo to Zr or Ti ratio is between about 1:1 to 1:10. A support typically serves as a binder for the catalyst resulting in a harder and more attrition resistant catalyst. However, for commercial applications, an appropriate blend of both the active phase (i.e.
35 the complex of catalytic oxides described above) and the support is helpful to obtain an

acceptable activity and hardness (attrition resistance) for the catalyst. Directionally, any increase in the amount of the active phase decreases the hardness of the catalyst. The support comprises between 10 and 90 weight percent of the supported catalyst. Typically, the support comprises between 40 and 60 weight percent of the supported catalyst. In one embodiment of this invention, the support may comprise as little as about 10 weight percent of the supported catalyst. In one embodiment of this invention, the support may comprise as little as about 30 weight percent of the supported catalyst. In another embodiment of this invention, the support may comprise as much as about 70 weight percent of the supported catalyst.

Mixed Metal Oxide Catalyst Preparation

The method of making the catalyst to be used in this invention is not critical. Any method known in the art such as but not limited to hydrothermal synthesis methods and non-hydrothermal synthesis methods may be used.

In one or more embodiments, the mixed metal oxide catalyst may be prepared by the hydrothermal synthesis methods described herein. Hydrothermal synthesis methods are disclosed in U.S. Patent Application No. 2003/0004379 to Gaffney et al., Watanabe et al., "New Synthesis Route for Mo-V-Nb-Te mixed oxides catalyst for propane ammoxidation", Applied Catalysis A: General, 194-195, pp. 479-485 (2000), and Ueda et al., "Selective Oxidation of Light Alkanes over hydrothermally synthesized Mo-V-M-O (M=Al, Ga, Bi, Sb and Te) oxide catalysts.", Applied Catalysis A: General, 200, pp. 135-145, which are incorporated here by reference.

In general, the catalyst compositions described herein can be prepared by hydrothermal synthesis where source compounds (i.e. compounds that contain and/or provide one or more of the metals for the mixed metal oxide catalyst composition) are admixed in an aqueous solution to form a reaction medium and the reaction medium is reacted at elevated pressure and elevated temperature in a sealed reaction vessel for a time sufficient to form the mixed metal oxide. In one embodiment, the hydrothermal synthesis continues for a time sufficient to fully react any organic compounds present in the reaction medium, for example, solvents used in the preparation of the catalyst or any organic compounds added with any of the source compounds supplying the mixed metal oxide components of the catalyst composition.

The source compounds are reacted in the sealed reaction vessel at a temperature greater than 100 °C and at a pressure greater than ambient pressure. In one embodiment, the source compounds are reacted in the sealed reaction vessel at a temperature of at least about 125 °C, in another embodiment at a temperature of at least about 150 °C, and in

yet another embodiment at a temperature of at least about 175 °C. In one embodiment, the source compounds are reacted in the sealed reaction vessel at a pressure of at least about 25 psig, and in another embodiment at a pressure of at least about 50 psig, and in yet another embodiment at a pressure of at least about 100 psig. In one or more
5 embodiments, the source compounds are reacted in the sealed reaction vessel at a pressure of up to about 300 psig. Such sealed reaction vessels may be equipped with a pressure control device to avoid over pressurizing the vessel and/or to regulate the reaction pressure.

 The source compounds may be reacted by a protocol that comprises mixing the
10 source compounds during the reaction step. The particular mixing mechanism is not critical, and can include for example, mixing (e.g., stirring or agitating) the components during the reaction by any effective method. Such methods include, for example, agitating the contents of the reaction vessel, for example by shaking, tumbling or oscillating the component-containing reaction vessel. Such methods also include, for
15 example, stirring by using a stirring member located at least partially within the reaction vessel and a driving force coupled to the stirring member or to the reaction vessel to provide relative motion between the stirring member and the reaction vessel. The stirring member can be a shaft-driven and/or shaft-supported stirring member. The driving force can be directly coupled to the stirring member or can be indirectly coupled to the stirring
20 member (e.g., via magnetic coupling). The mixing is generally sufficient to allow for efficient reaction between components of the reaction medium, and to form a more homogeneous reaction medium (e.g., and resulting in a more homogeneous mixed metal oxide precursor) as compared to an unmixed reaction. This may result in more efficient consumption of starting materials and in a more uniform mixed metal oxide product.
25 Mixing the reaction medium during the reaction step also causes the mixed metal oxide product to form in solution rather than on the sides of the reaction vessel. This allows more ready recovery and separation of the mixed metal oxide product by techniques such as centrifugation, decantation, or filtration and avoids the need to recover the majority of product from the sides of the reactor vessel. More advantageously, having the mixed
30 metal oxide form in solution allows for particle growth on all faces of the particle rather than on the limited exposed faces when the growth occurs out from the reactor wall.

 It is generally desirable to maintain some headspace in the reactor vessel. The amount of headspace may depend on the vessel design or the type of agitation used if the reaction mixture is stirred. Overhead stirred reaction vessels, for example, may take 50%
35 headspace. Typically, the headspace is filled with ambient air which provides some

amount of oxygen to the reaction. However, the headspace, as is known the art, may be filled with other gases to provide reactants like O₂ or even an inert atmosphere such as Ar or N₂. The amount of headspace and gas within it depends upon the desired reaction as is known in the art.

5 The source compounds can be reacted in the sealed reaction vessel at an initial pH of not more than about 4. Over the course of the hydrothermal synthesis, the pH of the reaction mixture may change such that the final pH of the reaction mixture may be higher or lower than the initial pH. In one or more embodiments, the source compounds are reacted in the sealed reaction vessel at a pH of not more than about 3.5. In some
10 embodiments, the components can be reacted in the sealed reaction vessel at a pH of not more than about 3.0, of not more than about 2.5, of not more than about 2.0, of not more than about 1.5 or of not more than about 1.0, of not more than about 0.5 or of not more than about 0. In one or more embodiments, the pH may be from about 0.5 to about 4, in other embodiments, from about 0 to about 4, in yet other embodiments, from about 0.5 to
15 about 3.5. In some embodiments, the pH is from about 0.7 to about 3.3, and in certain embodiments, from about 1 to about 3. The pH may be adjusted by adding acid or base to the reaction mixture.

 The source compounds can be reacted in the sealed reaction vessels at the aforementioned reaction conditions (including for example, reaction temperatures,
20 reaction pressures, pH, stirring, etc., as described above) for a period of time sufficient to form the mixed metal oxide. In one or more embodiments, the mixed metal oxide thus formed comprises a solid state solution comprising the required elements as discussed above, and at least a portion thereof includes the requisite crystalline structure for active and selective propane or isobutane oxidation and/or ammoxidation catalysts. The exact
25 period of reaction time is not narrowly critical, and can include for example at least about three hours, at least about six hours, at least about twelve hours, at least about eighteen hours, at least about twenty-four hours, at least about thirty hours, at least about thirty-six hours, at least about forty-two hours, at least about forty-eight hours, at least about fifty-four hours, at least about sixty hours, at least about sixty-six hours or at least about
30 seventy-two hours. Reaction periods of time can be even more than three days, including for example at least about four days, at least about five days, at least about six days, at least about seven days, at least about two weeks, at least about three weeks, or at least about one month.

 Some source compounds containing and providing the metal components used in
35 the synthesis of the catalyst (also referred to herein as a "source" or "sources") may be

provided to the reaction vessel as aqueous solutions of the metal salts. Some source compounds may be provided to the reaction vessels as solids or as slurries comprising solid particulates dispersed in an aqueous media. Some source compounds may be provided to the reaction vessels as solids or as slurries comprising solid particulates dispersed in non-aqueous solvents or other non-aqueous media.

Examples of source compounds for synthesis of the catalysts as described herein include the following. Examples of lithium sources include lithium hydroxide, lithium oxide, lithium acetate, lithium tartrate, and lithium nitrate. Examples of vanadium sources include vanadyl sulfate, ammonium metavanadate, and vanadium(V) oxide. Examples of antimony sources include antimony(III) oxide, antimony(III) acetate, antimony(III) oxalate, antimony(V) oxide, antimony(III) sulfate, and antimony(III) tartrate. Examples of niobium sources include niobium oxalate, ammonium niobium oxalate, niobium oxide, niobium ethoxide and niobic acid.

Tungsten sources include ammonium metatungstate, tungstic acid, and tungsten trioxide. Tellurium sources include telluric acid, tellurium dioxide, tellurium trioxide, organic tellurium compounds such as methyltellurol and dimethyl tellurol.

Titanium sources include rutile and/or anatase titanium dioxide (TiO_2), titanium isopropoxide, $\text{TiO}(\text{oxalate})$, $\text{TiO}(\text{acetylacetonate})_2$, and titanium alkoxide complexes, such as Tyzor 131. Titanium dioxide is available as Degussa P-25, Tronox A-K-1, and Tronox 8602 (formerly named A-K-350). Tin sources include tin (II) acetate. Germanium sources include germanium(IV) oxide. Zirconium sources include zirconyl nitrate and zirconium (IV) oxide. Hafnium sources may include hafnium (IV) chloride and hafnium (IV) oxide.

Lanthanum sources include lanthanum (III) chloride, lanthanum (III) oxide, and lanthanum (III) acetate hydrate. Cerium sources include cerium (III) chloride, cerium (III) oxide, cerium (III) isopropoxide, and cerium (III) acetate hydrate. Praseodymium sources include praseodymium (III) chloride, praseodymium (III, IV) oxide, praseodymium (III) isopropoxide, and praseodymium (III) acetate hydrate. Neodymium sources include neodymium (III) chloride, neodymium (III) oxide, neodymium (III) isopropoxide, and neodymium (III) acetate hydrate. Samarium sources may include samarium (III) chloride, samarium (III) oxide, samarium (III) isopropoxide, and samarium (III) acetate hydrate. Europium sources may include europium (III) chloride, europium (III) oxide, and europium (III) acetate hydrate. Gadolinium sources may include gadolinium (III) chloride, gadolinium (III) oxide, and gadolinium (III) acetate hydrate. Terbium sources include terbium (III) chloride, terbium (III) oxide, and terbium

(III) acetate hydrate. Dysprosium sources may include dysprosium (III) chloride, dysprosium (III) oxide, dysprosium (III) isopropoxide, and dysprosium (III) acetate hydrate. Holmium sources may include holmium (III) chloride, holmium (III) oxide, and holmium (III) acetate hydrate. Erbium sources may include erbium (III) chloride, erbium (III) oxide, erbium (III) isopropoxide, and erbium (III) acetate hydrate. Thulium sources may include thulium (III) chloride, thulium (III) oxide, and thulium (III) acetate hydrate. Ytterbium sources may include ytterbium (III) chloride, ytterbium (III) oxide, ytterbium (III) isopropoxide, and ytterbium (III) acetate hydrate. Sources of lutetium may include lutetium (III) chloride, lutetium (III) oxide, and lutetium (III) acetate hydrate. Nitrates of the above listed metals may also be employed as source compounds.

The amount of aqueous solvent in the reaction medium may vary due to the solubilities of the source compounds combined to form the particular mixed metal oxide. The amount of aqueous solvent should at least be sufficient to yield a slurry (a mixture of solids and liquids which is able to be stirred) of the reactants. It is typical in hydrothermal synthesis of mixed metal oxides to leave an amount of headspace in the reactor vessel.

Following the reaction step, further steps of the catalyst preparation methods may include work-up steps, including for example cooling the reaction medium comprising the mixed metal oxide (e.g., to about ambient temperature), separating the solid particulates comprising the mixed metal oxide from the liquid (e.g., by centrifuging and/or decanting the supernatant, or alternatively, by filtering), washing the separated solid particulates (e.g., using distilled water or deionized water), repeating the separating step and washing steps one or more times, and effecting a final separating step. In one embodiment, the work up step comprises drying the reaction medium, such as by rotary evaporation, spray drying, freeze drying, or similar methods of removing liquid.

After the work-up steps, the washed and separated mixed metal oxide may be dried. Drying the mixed metal oxide can be effected under ambient conditions (e.g., at a temperature of about 25 °C at atmospheric pressure), and/or in an oven, for example, at a temperature ranging from about 40 °C to about 150 °C, and in one or more embodiments at about 120 °C over a drying time ranging from about five to about fifteen hours, and in one or more embodiments of about twelve hours. Drying can be effected under a controlled or uncontrolled atmosphere, and the drying atmosphere may be an inert gas, an oxidative gas, a reducing gas or air.

In one or more embodiments of this invention, the mixed metal oxide catalyst may be prepared by non-hydrothermal synthesis methods described herein. Non-

hydrothermal syntheses are also disclosed in US Patent Application No. 2006/0235238 to Satoru Komada and Sadao Shoji, and in WO 2006/019078 to Kato Takakai and Fukushima Satoshi, which are incorporated herein by reference.

One non-hydrothermal method may be generally described as follows. A first aqueous solution/slurry is prepared by combining, with heating and stirring, a molybdenum source compound, a vanadium source compound, an antimony source compound, optionally other source compounds, hydrogen peroxide, and a support sol, such as silica sol. A second aqueous solution/slurry is prepared by combining, with heating and stirring, a niobium source compound, optionally a dicarboxylic acid, and optionally other source compounds. The first and second aqueous solutions/slurries are combined to form a third aqueous solution/slurry. Precipitate and/or suspended solids may be removed, and the aqueous mixture is dried to form a dry mixed metal oxide catalyst. Various work-up steps and methods of drying and/or calcination may be employed.

In one embodiment, a non-hydrothermal method may be more specifically described as follows, where the first aqueous solution/slurry is denoted (A), and the second aqueous solution/slurry is denoted (B). Ammonium heptamolybdate, ammonium metavanadate and diantimony trioxide are added to water, followed by heating of the resultant mixture to temperatures of at least 50° C, thereby obtaining an aqueous mixture (A). It is preferred that the heating is performed while stirring the mixture. Advantageously the aqueous mixture is heated to temperatures in the range of from about 70° C to the normal boiling point of the mixture. The heating may be performed under reflux by using equipment having a reflux condenser. In the case of heating under reflux, the boiling point generally is in the range of from about 101° C to 102° C. Elevated temperatures may be maintained for about 0.5 hours or more. When the heating temperature is from about 80° C to about 100° C, the heating time is typically from about 1 to about 5 hours. When the heating temperature is relatively low (e.g., lower than about 50° C), the heating time needs to be longer.

Optionally, hydrogen peroxide and/or a sol of support material, such as silica sol, may be added to the aqueous mixture (A) after heating as described above. When hydrogen peroxide is added to the aqueous mixture (A), the amount of the hydrogen peroxide may be such that the molar ratio of hydrogen peroxide to antimony ($\text{H}_2\text{O}_2/\text{Sb}$ molar ratio) compound in terms of antimony is in the range of from about 0.01 to about 20, in one embodiment, in the range of from about 0.5 to about 3, in another embodiment, in the range of from about 1 to about 2.5. After addition of hydrogen

peroxide, aqueous mixture (A) may be stirred at temperatures in the range of from about 30° C to about 70° C for from about 30 minutes to about 2 hours.

In one or more embodiments, aqueous solution/slurry (B) may be formed by combining water, a niobium source compound, optionally dicarboxylic acid and/or other source compounds, with heating and stirring, thereby obtaining a preliminary niobium-containing aqueous solution or niobium-containing aqueous mixture having suspended therein a part of the niobium compound. The preliminary niobium-containing aqueous solution or niobium-containing aqueous mixture may then be cooled, whereby if a dicarboxylic acid was added, a portion of it may precipitate. The step of cooling may be followed by removing the precipitated dicarboxylic acid from the preliminary niobium-containing aqueous solution, or removing the precipitated dicarboxylic acid and the suspended niobium compound from the niobium-containing aqueous mixture, thereby obtaining a niobium-containing aqueous liquid (B).

In one embodiment, an aqueous liquid (B) may be obtained by adding a niobium compound (e.g., niobic acid) to water, followed by heating of the resultant mixture to temperatures in a range of from about 50° C to about 100° C. Where niobic acid is the niobium source compound, a dicarboxylic acid may also be added. Dissolution of the niobium compound may be promoted by the addition of a small amount of aqueous ammonia.

Examples of suitable dicarboxylic acids include oxalic acid. In one embodiment, niobic acid and oxalic acid are added to water, followed by heating and stirring of the resultant mixture to thereby obtain an aqueous liquid (B). Generally, the molar ratio of the dicarboxylic acid to the niobium compound in terms of niobium is in the range of from about 1 to about 4, in one embodiment, in the range of from about 2 to about 4.

In other embodiments, the niobium source compound includes niobium hydrogenoxalate or ammonium niobium oxalate. When either niobium hydrogenoxalate or ammonium niobium oxalate is used as the niobium compound, the dicarboxylic acid is not required.

In general, the niobium source compound may be added in the form of a solid, a mixture, or as a dispersion in an appropriate medium. When niobic acid is used as the niobium compound, in order to remove acidic impurities with which the niobic acid may have been contaminated during the production thereof, the niobic acid may be washed with an aqueous ammonia solution and/or water prior to use. It may be advantageous to use, as the niobium compound, a freshly prepared niobium compound. However, a niobium compound that is slightly denatured (for example by dehydration) as a result of

a long-term storage and the like, may be used.

The concentration of the niobium compound (in terms of niobium) in the preliminary niobium-containing aqueous solution or aqueous mixture is, in one or more embodiments, maintained within the range of from about 0.2 to about 0.8 mol/kg of the solution or mixture. The dicarboxylic acid is, in one or more embodiments, used in an amount such that the molar ratio of dicarboxylic acid to niobium compound in terms of niobium is from about 2 to about 6. When an excess amount of the dicarboxylic acid is used, a large amount of the niobium compound can be dissolved in the aqueous solution of dicarboxylic acid; however, the amount of the dicarboxylic acid that precipitates upon cooling the obtained preliminary niobium-containing aqueous solution or mixture may become too large, thus decreasing the utilization of the dicarboxylic acid. On the other hand, when an inadequate amount of the dicarboxylic acid is used, a large amount of the niobium compound may remain undissolved and suspended in the aqueous solution or mixture, and as such may be subsequently removed from the aqueous mixture, thus decreasing the degree of utilization of the niobium compound.

Any suitable method of cooling may be used. For example, the cooling can be performed simply by means of an ice bath.

The removal of the precipitated dicarboxylic acid (or precipitated dicarboxylic acid and the dispersed niobium compound) can be easily performed by conventional methods, for example, by decantation or filtration.

When the dicarboxylic acid/niobium molar ratio of the obtained niobium-containing aqueous solution is outside the range of from about 2 to about 6, either the niobium compound or dicarboxylic acid may be added to the aqueous liquid (B) so that the dicarboxylic acid/niobium molar ratio of the solution falls within the above-mentioned range. However, in general, such an operation is unnecessary since an aqueous liquid (B) having the dicarboxylic acid/niobium molar ratio within the range of from about 2 to about 4 can be prepared by appropriately controlling the concentration of the niobium compound, the ratio of the dicarboxylic acid to the niobium compound and the cooling temperature of the above-mentioned preliminary niobium-containing aqueous solution or aqueous mixture.

The aqueous liquid (B) may further comprise additional component(s). In one or more embodiments, aqueous liquid (B) may further comprise hydrogen peroxide (H_2O_2). In these or other embodiments, aqueous liquid (B) may further comprise one or more of an antimony compound (e.g. diantimony trioxide), a titanium compound (e.g. titanium dioxide, which can be a mixture of rutile and anatase forms), and a cerium compound

(e.g. cerium acetate). In one embodiment, the amount of the hydrogen peroxide is such that the molar ratio of hydrogen peroxide to niobium compound ($\text{H}_2\text{O}_2/\text{Nb}$ molar ratio) in terms of niobium is in the range of from about 0.5 to about 20, and in another embodiment, in the range of from about 1 to about 20. In certain embodiments, an
5 antimony compound is mixed with at least a part of the aqueous liquid (B) and the hydrogen peroxide such that the molar ratio (Sb/Nb molar ratio) of the antimony compound in terms of antimony to the niobium compound in terms of niobium is not more than about 5, and in one embodiment, in the range of from about 0.01 to about 2.

Aqueous mixture (A) and aqueous liquid (B) may be mixed together in an
10 appropriate ratio to form an aqueous solution/slurry. The ratio of (a) to (b) will be in accordance with the desired composition of the catalyst. The amount of solids in the aqueous mixture is generally in a range upward from about 10 percent by weight. In one embodiment, the amount of solids in the aqueous mixture is from about 10 to 60 percent by weight, in another embodiment, from about 15 to 55 percent by weight, and in
15 another embodiment, the amount of solids in the mixture is from about 20 to about 50 percent by weight, based upon the total weight of the mixture.

In one or more embodiments, where a silica supported catalyst is desired, the aqueous solution/slurry is prepared so as to contain a source of silica (namely, a silica sol or fumed silica). The amount of the source of silica may be appropriately adjusted in
20 accordance with the desired amount of the silica carrier in the catalyst to be obtained.

The aqueous solution/slurry may be dried to remove the liquid portion. Drying may be conducted by conventional methods, such as spray drying or evaporation drying. Spray drying is particularly useful, because a fine, spherical, dry solid is obtained. The spray drying can be conducted by centrifugation.

25 The aqueous solution/slurry may be dried to remove the liquid portion. Drying may be conducted by conventional methods, such as spray drying or evaporation drying. Spray drying is particularly useful, because a fine, spherical, dry solid is obtained. The spray drying can be conducted by centrifugation, by the two-phase flow nozzle method or by the high-pressure nozzle method. As a heat source for drying, it is preferred to use
30 air which has been heated by steam, an electric heater and the like. It may be advantageous if the temperature of the spray dryer at an entrance to the dryer section thereof is from about 150°C to about 300°C .

At this point, the dried material, whether formed via hydrothermal or nonhydrothermal methods, may be referred to as dry mixed metal oxide catalyst. It will
35 be understood that the terms "dry" and "dried" describe a solid from which most liquid

has been removed, although some moisture may remain. Therefore, unless otherwise indicated, the terms "dry" and "dried" should be interpreted to mean substantially dry. For purposes of this specification, the term "dry mixed metal oxide catalyst" continues to refer to this substance throughout optional further treatments to which the dry mixed metal oxide catalyst may be subjected, including calcination and grinding, as described hereinbelow. Additionally, the term "dry mixed metal oxide catalyst" may refer to catalyst that has been used in a reactor. Thus, a dry mixed metal oxide catalyst may be calcined or uncalcined, ground, crushed, pelleted, extruded, or otherwise formed or shaped, and may be fresh catalyst or used.

As stated hereinabove, the dried mixed metal oxide catalyst may be further treated. Such treatments can include for example calcinations (e.g., including heat treatments under oxidizing or reducing conditions) effected under various treatment atmospheres. The dry mixed metal oxide can be crushed or ground prior to such treatment, and/or intermittently during such treatment. In one embodiment, for example, the dry mixed metal oxide can be optionally crushed, and then calcined.

The calcination may be effected in an inert, reducing, or oxidizing atmosphere. In one embodiment, at least a part of the calcination is conducted in an atmosphere of an inert gas (e.g., under a flow of an inert gas), such as nitrogen gas that is substantially free of oxygen. In one or more embodiments, the calcination conditions include temperatures ranging from about 200 °C to about 700 °C, in other embodiments, from about 400 °C to about 650 °C.

In one or more embodiments, the heating temperature of the dry mixed metal oxide catalyst is continuously or intermittently elevated from less than about 400° C to from about 550° C to about 700° C. In certain embodiments, multi-step calcination may be employed. In these embodiments, the dry mixed metal oxide catalyst may be partially calcined at a relatively low temperature of at least about 200 °C, and then at one or more higher temperatures of at least about 400 °C, within the ranges set forth hereinabove.

The treated (e.g., calcined) mixed metal oxide may be further mechanically treated, including for example by grinding, sieving and pressing the mixed metal oxide into its final form for use in the process of the present invention.

In other embodiments, the catalyst may be shaped into its final form prior to any calcinations or other heat treatment. For example, in the preparation of a fixed bed catalyst, the catalyst precursor slurry is typically dried by heating at an elevated temperature and then shaped (e.g. extruded, pelletized, etc.) to the desired fixed bed catalyst size and configuration prior to calcination. Similarly, in the preparation of fluid

bed catalysts, the catalyst precursor slurry may be spray dried to yield microspheroidal catalyst particles having particle diameters in the range from about 10 to about 200 microns and then calcined. Variations on the above methods will be recognized by those skilled in the art.

5 Calcinations can be conducted using a rotary kiln, a fluidized-bed kiln or the like. In one or more embodiments, calcination is conducted in a non-stationary state, and problems of uneven calcination (leading to a deterioration of the properties and/or a breakage or cracking of the catalyst obtained) are avoided.

 Conditions of calcination may be preselected such that the catalyst formed has a
10 specific surface of from about 5 m²/g to about 35 m²/g. Advantageously, the conditions of calcination may be preselected such that the resulting catalyst comprises one or more crystalline phases.

Method of Forming Physical Mixture

 The catalyst mixture may be prepared by combining the fresh catalyst
15 composition, used catalyst composition, and performance modifier via physical mixing, wet impregnation, or some combination of these techniques. One or more of the components may be pre-mixed. The order of addition is not critical. In one embodiment, the performance modifier and fresh catalyst may be pre-mixed, and then mixed with the used catalyst. The performance modifier may be added at various stages of the
20 preparation of the fresh catalyst composition. However, in certain embodiments performance improvement is seen where the modifier is added to the final form of the fresh catalyst composition.

 In one embodiment, the performance modifier and used catalyst may be pre-mixed, and then mixed with the fresh catalyst. In one embodiment, the performance
25 modifier is a solid, and may be finely ground prior to combining the modifier with the catalyst compositions. In another embodiment, the performance modifier has a more coarse particle size, *i.e.* on the order of the particle size of the catalyst.

 In one or more embodiments, the performance modifier may be added to one or both of the used and fresh catalyst compositions via wet impregnation methods. In one
30 embodiment, the physical mixture of performance modifier, fresh mixed oxide catalyst, and used mixed oxide catalyst may be subjected to a heat treatment or calcination.

 In certain embodiments, where two or more performance modifier compounds are employed, the performance modifier compounds may be added to the catalyst mixture separately, or may be pre-mixed to form a modifier mixture. The modifier
35 mixture may then be mixed with the mixed oxide catalyst compositions via physical

mixing or impregnation.

Conversion of Propane and Isobutane via Ammoxidation and Oxidation Reaction

The present invention provides a process for converting propane to acrylonitrile and isobutane to methacrylonitrile. The process includes preparing a mixture of a performance modifier, a fresh mixed oxide catalyst composition, and a used mixed oxide catalyst composition as described hereinabove, and contacting the catalyst mixture with propane or isobutane in the presence of oxygen (e.g. provided to the reaction zone in a feedstream comprising an oxygen-containing gas, such as and typically air) and ammonia under reaction conditions effective to form acrylonitrile or methacrylonitrile.

For this reaction, the feed stream comprises propane or isobutane, an oxygen-containing gas such as air, and ammonia. In one or more embodiments, the molar ratio of propane or isobutane to oxygen is from about 0.125 to about 5, in another embodiment, from about 0.25 to about 4.5, and in another embodiment, from about 0.35 to about 4. In one or more embodiments, the molar ratio of propane or isobutane to ammonia is from about 0.3 to about 4, and in another embodiment, from about 0.5 to about 3. The feed stream can also comprise one or more additional feed components, including acrylonitrile or methacrylonitrile product (e.g., from a recycle stream or from an earlier-stage of a multi-stage reactor), and/or steam. For example, the feedstream can comprise from about 5% to about 30% by weight of additional feed components, relative to the total amount of the feed stream, or by mole relative to the amount of propane or isobutane in the feed stream. In one embodiment the process described herein for the ammoxidation of propane to acrylonitrile is a once-through process, i.e., it operates without recycle of recovered but unreacted feed materials.

Propane can also be converted to acrylic acid and isobutane to methacrylic acid by providing one or more of the aforementioned catalysts in a gas-phase flow reactor, and contacting the catalyst with propane in the presence of oxygen (e.g. provided to the reaction zone in a feedstream comprising an oxygen-containing gas, such as and typically air) under reaction conditions effective to form acrylic acid. The feed stream for this reaction preferably comprises propane or isobutane to oxygen ranging from about 0.15 to about 5, and preferably from about 0.25 to about 2. The feed stream can also comprise one or more additional feed components, including acrylic acid or methacrylic acid product (e.g. from a recycle stream or from an earlier-stage of a multi-stage reactor), and/or steam. For example, the feedstream can comprise about 5% to about 30% by weight relative to the total amount of the feed stream, or by mole relative to the amount of propane isobutane in the feed stream.

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may vary slightly from the nominal compositions shown below.

Fresh catalyst was prepared in its final form, according to methods described herein. A portion of the fresh catalyst was combined with used catalyst and a catalyst modifier and mixed in a dry state, by using a mechanical mixer.

- 5 Catalyst was evaluated in a 40 cc fluid bed reactor having a diameter of 1-inch. The reactor was charged with about 20 to about 45g of particulate catalyst or catalyst mixture. Propane was fed into the reactor at a rate of about 0.04 to about 0.15 WWH (i.e., weight of propane/weight of catalyst/hour). Generally, ammonia was fed into the reactor at a flow rate such that ammonia to propane ratio was from about 1 to about 1.5.
- 10 Pressure inside the reactor was maintained at about 2 to about 15 psig. Reaction temperatures were in the range of about 420 to about 460 °C.

Comparative Example 1 – A catalyst was prepared having the nominal composition: $\text{MoV}_{0.21}\text{Sb}_{0.24}\text{Nb}_{0.09}\text{O}_x$, and including 45 % by weight silica support. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 1.

- 15 Example 1-1 – The used catalyst of Comparative Example 1 was combined with fresh catalyst having the nominal composition $\text{MoV}_{0.21}\text{Sb}_{0.24}\text{Nb}_{0.09}\text{O}_x$ in a ratio of 2/3 used catalyst to 1/3 fresh catalyst and also combined with Sb_2O_3 in an amount of 0.1 moles of Sb per mole Mo in the base catalyst composition. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 1.

- 20 Comparative Example 2 – A catalyst was prepared having the same nominal composition as Comparative Example 1. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 1.

- Example 2-1 – The used catalyst of Comparative Example 2 was combined with fresh catalyst having the nominal composition $\text{MoV}_{0.21}\text{Sb}_{0.24}\text{Nb}_{0.09}\text{O}_x$ in a ratio of 2/3
- 25 used catalyst to 1/3 fresh catalyst and also combined with MoO_3 in an amount of 0.02 moles of Mo per mole Mo in the base catalyst composition. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 1.

- Example 2-2 – The used catalyst of Example 2-1 was combined with fresh catalyst having the nominal composition $\text{MoV}_{0.21}\text{Sb}_{0.24}\text{Nb}_{0.09}\text{O}_x$ in a ratio of 2/3 used
- 30 catalyst to 1/3 fresh catalyst and also combined with Sb_2O_3 in an amount of 0.1 moles of Sb per mole Mo in the base catalyst composition. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 1.

Table 1

Example No.	WWH	Press., psig	Temp., °C	Propane Conv., %	Acrylonitrile Sel., %	Acrylonitrile Yield, %	HCN Yield, %	Acetonitrile Yield, %	Acrylic Acid Yield, %	CO ₂ Yield, %	CO Yield, %	Hours on Stream
Comparative Example 1	0.060	10	439	76.0	48.8	37.1	4.7	2.0	3.0	14.3	12.9	19
	0.060	10	439	76.8	49.4	37.9	4.9	2.1	2.1	14.7	13.3	20
	0.060	10	439	76.7	49.4	37.9	4.8	2.1	2.5	14.5	13.1	21
Example 1-1	0.060	10	440	79.8	50.1	39.9	4.7	2.3	2.6	14.9	13.7	17
	0.060	10	440	80.2	49.8	39.9	4.8	2.3	2.7	15.2	13.7	20
Comparative Example 2	0.06	10	440	71.1	46.2	32.9	4.6	3	1.7	15.2	11.8	16
	0.06	10	439	71.1	46.4	33	4.6	3	1.7	15.2	11.6	18
Example 2-1	0.06	10	441	73.4	45.1	33.1	4.7	2.8	1.6	15.7	13.6	16
	0.06	10	440	74.2	45.1	33.4	4.7	2.8	2.1	15.8	13.2	18.5
Example 2-2	0.06	10	440	74.4	46.4	34.5	4.8	2.5	1.2	15.7	13.7	16

Comparative Example 3 – A catalyst was prepared having the nominal composition: $\text{MoV}_{0.21}\text{Sb}_{0.24}\text{Nb}_{0.09}\text{O}_x$, and including 45 % by weight silica support. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 2.

Example 3-1 – The catalyst of Comparative Example 3 was combined with 0.05 moles of Sb_2O_3 per mole Mo in the base catalyst composition. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 2.

Example 3-2 – The catalyst of Comparative Example 3 was combined with 0.1 moles of Sb_2O_3 per mole Mo in the base catalyst composition. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 2.

Example 3-3 – The catalyst of Comparative Example 3 was combined with 0.2 moles of Sb_2O_3 per mole Mo in the base catalyst composition. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 2.

Example 3-4 – The catalyst of Comparative Example 3 was combined with 0.02 moles of TiO_2 per mole Mo in the base catalyst composition. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 2.

Example 3-5 – The catalyst of Comparative Example 3 was combined with 0.02 moles H_6TeO_6 per mole Mo in the base catalyst composition. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 2.

Example 3-6 – The catalyst of Comparative Example 3 was combined with 0.1 moles of Sb_2O_3 per mole Mo. The catalyst was evaluated in a 40 cc fluid bed reactor. Catalyst performance after an extended time on-stream is summarized in Table 2.

Example 3-7 – The catalyst of Comparative Example 3 was combined with 0.05 moles of H_3BO_3 per mole Mo in the base catalyst composition. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 2.

Example 3-8 – The catalyst of Comparative Example 3 was combined with 0.1 moles of Sb_2O_4 per mole Mo. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 2.

Example 3-9 – The catalyst of Comparative Example 3 was combined with 0.05 moles of $(\text{NH}_4)_2\text{HPO}_4$ per mole Mo. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 2.

Example 3-10 – The catalyst of Comparative Example 3 was combined with 0.04 moles of LiOH per mole Mo in the base catalyst composition. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 2.

Table 2

Example	WWH	Press., psig	Temp., °C	Propane Conv., %	Acrylonitrile Sel., %	Acrylonitrile Yield, %	HCN Yield, %	Acetonitrile Yield, %	Acrylic Acid Yield, %	CO_2 Yield, %	CO Yield, %	Hours on Stream
Comparative Example 3	0.049	10	440	79.7	45.3	36.1	4.7	2.4	1.7	18.6	14.8	22.0
Example 3-1	0.049	10	440	78.7	49.5	39.0	4.5	2.6	2.4	16.1	12.8	20.0
	0.049	10	440	79.3	49.1	38.9	4.6	2.6	2.2	16.3	13.2	22.0
Example 3-2	0.049	10	440	81.6	51.1	41.7	4.3	2.7	1.9	16.5	13.3	17.0
	0.049	10	440	81.7	50.8	41.5	4.3	2.6	2.4	16.4	13.2	18.0
Example 3-3	0.049	10	440	79.6	49.4	39.3	4.5	2.5	1.9	16.8	13.0	17.0
Example 3-4	0.060	10	440	85.3	44.3	37.8	4.6	2.4	2.0	19.8	17.7	26
Example 3-5	0.049	10	440	79.6	48.0	38.2	3.8	1.9	2.7	16.3	15.2	16
Example 3-6	0.06	10	439	78.6	52.1	41	5	2.6	1.5	14.7	12.2	90
	0.06	10	439	78.9	51.8	40.8	5.2	2.6	1.6	14.7	12.3	94
Example 3-7	0.06	10	440	71.1	53.9	38.3	4.1	2.8	2.6	11.5	9.8	16
Example 3-8	0.06	10	440	80.2	51	40.9	4.5	2.6	3.4	14.1	12.8	15
	0.06	10	440	80.8	51.7	41.7	4.6	2.7	3.1	14.2	12.8	18
Example 3-9	0.06	10	440	73.3	37.3	27.4	2.9	2.1	9.1	12.6	16	15
Example 3-10	0.06	10	440	78.2	51.5	40.2	5.4	2.7	1.2	16.1	11	16
	0.06	10	440	78.5	50.8	39.9	5.4	2.6	1.9	16	11.1	19

Comparative Example 4 – A catalyst was prepared having the nominal composition $\text{MoV}_{0.3}\text{Sb}_{0.2}\text{Nb}_{0.08}\text{Ti}_{0.1}\text{Ce}_{0.005}\text{O}_x$, and including 45 % by weight silica support. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 3.

5 Example 4-1 – The catalyst of Comparative Example 4 was combined with 0.025 moles of GeO_2 per mole Mo in the base catalyst composition. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 3.

10 Example 4-2 – The catalyst of Comparative Example 4 was combined with 0.025 moles of CeO_2 per mole Mo in the base catalyst composition. The catalyst was evaluated in a 40 cc fluid bed reactor. The results are shown in Table 3.

Table 3

Example	Wt%	Press., psig	Temp., °C	Propane Conv., %	Acrylonitrile Sel., %	Acrylonitrile Yield, %	HCN Yield, %	Acetonitrile Yield, %	Acrylic Acid Yield, %	CO ₂ Yield, %	CO Yield, %	Hours on Stream
Comparative Example 4	0.060	10	440	84.3	44.9	37.8	5.7	2.7	1.1	20.6	15.2	17
Example 4-1	0.060	10	440	83.4	48.9	40.8	5.1	3.4	2.3	16.6	13.8	17
	0.060	10	440	83.3	48.8	40.7	5.2	3.3	1.9	16.9	14.0	19
Example 4-2	0.060	10	440	82.5	49.2	40.5	5.1	3.4	2.2	15.5	14.1	17

15 While the foregoing description and the above embodiments are typical for the practice of the instant invention, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of this description. Accordingly, it is intended that all such alternatives, modifications and variations are embraced by and fall within the spirit and broad scope of the appended claims.

CLAIMS

We claim:

1. A process for the ammoxidation or oxidation of a saturated or unsaturated
5 or mixture of saturated and unsaturated hydrocarbon to produce an unsaturated nitrile or
an unsaturated organic acid, said process comprising:
providing a catalyst mixture comprising
a fresh mixed metal oxide catalyst comprising molybdenum, vanadium, niobium,
and at least one element selected from the group consisting of antimony and tellurium,
10 a used mixed metal oxide catalyst comprising molybdenum, vanadium, niobium,
and at least one element selected from the group consisting of antimony and tellurium,
and
a performance modifier selected from the group consisting of aluminum
compounds, antimony compounds, arsenic compounds, boron compounds, cerium
15 compounds, germanium compounds, lithium compounds, neodymium compounds,
niobium compounds, phosphorus compounds, selenium compounds, tantalum
compounds, tellurium compounds, titanium compounds, tungsten compounds, vanadium
compounds, zirconium compounds, and mixtures thereof; and
contacting the saturated or unsaturated or mixture of saturated and unsaturated
20 hydrocarbon with an oxygen-containing gas, or with an oxygen-containing gas and
ammonia, in the presence of the catalyst mixture.
2. The process of claim 1, wherein the catalyst modifier is selected from the
group consisting of aluminum nitrate, alumina, antimony(III) oxide, antimony(III)
25 oxalate, antimony (III) tartrate, antimony(V) oxide, antimony tetroxide, Sb_6O_{13} ,
arsenic(III) oxide, arsenic(V) oxide, arsenic acid, boron oxide, boric acid, ceric
ammonium nitrate, cerium acetate, cerium(III) oxalate hydrate, cerium(IV) oxide,
germanium(IV) oxide, lithium oxide, lithium hydroxide, lithium acetate, lithium nitrate,
lithium tartrate, ammonium niobium oxalate, niobium oxalate niobium oxide,
30 phosphorus pentoxide, ammonium phosphate, selenium dioxide, tantalum(V) oxide,
telluric acid, tellurium dioxide, tellurium trioxide, rutile titanium dioxide (TiO_2), anatase
titanium dioxide (TiO_2), titanium isopropoxide, $\text{TiO}(\text{oxalate})$, tungsten trioxide, vanadyl
oxalate, vanadium (III) oxide, vanadium (IV) oxide, vanadium(V) oxide, zirconyl nitrate,
zirconia, and mixtures thereof.

35

3. The process of claim 1, wherein one or more of the performance modifier, the fresh mixed metal oxide catalyst, and the used mixed metal oxide catalyst comprises a support selected from the group consisting of silica, alumina, zirconia, titania, or mixtures thereof.

5

4. The process of claim 1, wherein the catalyst mixture comprises at least about 0.01 moles of performance modifier per mole of Mo in the total amount of fresh and used mixed metal oxide catalyst.

10

5. The process of claim 1, wherein the performance modifier further comprises a molybdenum compound.

6. The process of claim 1, wherein one or both of the fresh mixed oxide catalyst and the used mixed oxide catalyst are prepared by using a non-hydrothermal synthesis method.

15

7. The process of claim 1, wherein the fresh catalyst composition comprises a mixed oxide defined by the empirical formula:



20

wherein X is selected from the group consisting of W, Te, Ti, Sn, Ge, Zr, Hf, Li, and mixtures thereof; L is selected from the group consisting of Ce, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and mixtures thereof; $0.1 \leq a \leq 1.0$, $0.01 \leq b \leq 1.0$, $0.001 \leq c \leq 0.25$, $0 \leq d \leq 0.6$, $0 \leq e \leq 1$; n is the number of oxygen atoms required to satisfy valance requirements of all other elements present in the mixed oxide with the proviso that one or more of the other elements in the mixed oxide can be present in an oxidation state lower than its highest oxidation state, a, b, c, d, and e represent the molar ratio of the corresponding element to one mole of Mo.

25

8. The process of claim 1, wherein the used catalyst composition comprises a mixed oxide defined by the empirical formula:

30



wherein X is selected from the group consisting of W, Te, Ti, Sn, Ge, Zr, Hf, Li, and mixtures thereof; L is selected from the group consisting of Ce, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and mixtures thereof; $0.1 \leq a \leq 1.0$, $0.01 \leq b \leq 1.0$, $0.001 \leq c \leq 0.25$, $0 \leq d \leq 0.6$, $0 \leq e \leq 1$; n is the number of oxygen atoms required to

35

satisfy valance requirements of all other elements present in the mixed oxide with the proviso that one or more of the other elements in the mixed oxide can be present in an oxidation state lower than its highest oxidation state, a, b, c, d, and e represent the molar ratio of the corresponding element to one mole of Mo.

5

9. The process of claim 1, wherein the performance modifier comprises antimony (III) oxide, antimony(III) oxalate, antimony (III) tartrate, antimony(V) oxide, antimony tetroxide, Sb_6O_{13} , germanium (IV) oxide, telluric acid, lithium hydroxide, or cerium (IV) oxide or a mixture thereof.

10

10. The process of claim 1, wherein said step of providing comprises physically mixing the fresh mixed oxide catalyst, the used fresh mixed oxide catalyst, and the performance modifier.

15

11. The process of claim 10, wherein said step of providing further comprises the step of pre-mixing the fresh mixed oxide catalyst composition and the performance modifier.

12. The process of claim 1, wherein said step of providing comprises
20 combining a fresh mixed oxide catalyst and a performance modifier via wet impregnation.

13. The process of claim 1, wherein said step of providing further comprises the step of heating or calcining said catalyst mixture.

25

14. A process for the ammoxidation or oxidation of a saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon to produce an unsaturated nitrile or an unsaturated organic acid, said process comprising:

physically mixing a dry mixed metal oxide catalyst and a performance modifier
30 to form a catalyst mixture, wherein the mixed metal oxide catalyst comprises molybdenum, vanadium, niobium, and at least one element selected from the group consisting of antimony and tellurium, and wherein the performance modifier is selected from the group consisting of aluminum compounds, antimony compounds, arsenic compounds, boron compounds, cerium compounds, germanium compounds, lithium
35 compounds, neodymium compounds, niobium compounds, phosphorus compounds,

selenium compounds, tantalum compounds, titanium compounds, tungsten compounds, vanadium compounds, zirconium compounds, and mixtures thereof; and

contacting the saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon with an oxygen-containing gas, or with an oxygen-containing gas and ammonia, in the presence of the catalyst mixture.

15. The process of claim 14, wherein the performance modifier is selected from the group consisting of aluminum nitrate, alumina, antimony(III) oxide, antimony(III) oxalate, antimony (III) tartrate, antimony(V) oxide, antimony tetroxide, Sb₆O₁₃, arsenic(III) oxide, arsenic(V) oxide, arsenic acid, boron oxide, boric acid, ceric ammonium nitrate, cerium acetate, cerium(III) oxalate hydrate, cerium(IV) oxide, germanium(IV) oxide, lithium oxide, lithium hydroxide, lithium acetate, lithium nitrate, lithium tartrate, neodymium (III) chloride, neodymium (III) oxide, neodymium (III) isopropoxide, neodymium (III) acetate hydrate, ammonium niobium oxalate, niobium oxalate niobium oxide, phosphorus pentoxide, ammonium phosphate, selenium dioxide, tantalum(V) oxide, rutile titanium dioxide (TiO₂), anatase titanium dioxide (TiO₂), titanium isopropoxide, TiO(oxalate), tungsten trioxide, vanadyl oxalate, vanadium (III) oxide, vanadium (IV) oxide, vanadium(V) oxide, zirconyl nitrate, zirconia, and mixtures thereof.

20

16. The process of claim 14, wherein the mixed metal oxide catalyst further comprises at least one element selected from the group consisting of lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, tungsten, titanium, tin, germanium, zirconium, lithium, and hafnium.

25

17. The process of claim 14, wherein one or more of the mixed metal oxide catalyst and the performance modifier comprises a support selected from the group consisting of silica, alumina, zirconia, titania, or mixtures thereof.

30

18. The process of claim 14, wherein the catalyst mixture comprises at least about 0.01 moles of performance modifier per mole of Mo in the mixed metal oxide catalyst.

35

19. The process of claim 14, wherein said step of physically mixing comprises mixing a calcined mixed metal oxide catalyst and a performance modifier.

20. The process of claim 14, wherein the mixed metal oxide catalyst
5 comprises a mixed oxide defined by the empirical formula:



wherein X is selected from the group consisting of W, Te, Ti, Sn, Ge, Zr, Hf, Li, and mixtures thereof; L is selected from the group consisting of Ce, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and mixtures thereof; $0.1 \leq a \leq 1.0$, $0.01 \leq b \leq 1.0$,
10 $0.001 \leq c \leq 0.25$, $0 \leq d \leq 0.6$, $0 \leq e \leq 1$; n is the number of oxygen atoms required to satisfy valance requirements of all other elements present in the mixed oxide with the proviso that one or more of the other elements in the mixed oxide can be present in an oxidation state lower than its highest oxidation state, a, b, c, d, and e represent the molar ratio of the corresponding element to one mole of Mo.

15

21. The process of claim 14, wherein the performance modifier comprises antimony (III) oxide, antimony(III) oxalate, antimony (III) tartrate, antimony(V) oxide, antimony tetroxide, Sb_6O_{13} , or a mixture thereof.

20 22. The process of claim 14, wherein the performance modifier further comprises a tellurium compound.

23. The process of claim 14, for the ammoxidation of a saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon, wherein said step of
25 contacting comprises contacting the saturated or unsaturated or mixture of saturated and unsaturated hydrocarbon with ammonia and an oxygen-containing gas in the presence of the catalyst mixture.

24. The process of claim 14, wherein the dry mixed metal oxide catalyst is
30 prepared by a non-hydrothermal synthesis method.

25. The process of claim 14, wherein said step of physically mixing comprises mixing an un-calcined or partially calcined dry mixed metal oxide catalyst and a performance modifier to form a mixture, and further comprises the step of calcining the
35 mixture.