MIXED OXIDE CATALYST OF RB, CE, CR, NI, FE, BI AND MO FOR THE MANUFACTURE OF ACRYLONITRILE

The present invention relates to an improved catalyst for use in the ammoxidation of an unsaturated hydrocarbon to the corresponding unsaturated nitrile. In particular, the present invention is directed to an improved process and catalyst for the ammoxidation of propylene and/or isobutylene to acrylonitrile and/or methacrylonitrile, respectively. More specifically, the invention relates to a novel and improved ammoxidation catalyst comprising a complex of catalytic oxides of iron, bismuth, molybdenum, magnesium, at least one of nickel or nickel and cobalt, rubidium, cerium, and chromium, in the substantial absence of any of manganese, a noble metal and vanadium.

Description of the Prior Art

Catalysts containing oxides of iron, bismuth and molybdenum, promoted with suitable elements, have long been used for the conversion of propylene at elevated temperatures in the presence of ammonia and oxygen (usually in the form of air) to manufacture acrylonitrile. In particular, Great Britain Patent 1436475; U.S. Patent Nos. 4,766,232; 4,377,534; 4,040,978; 4,168,246; 5,223,469 and 4,863,891 are each directed to bismuth-molybdenum-iron catalysts, which may be promoted with the Group II elements to produce acrylonitrile. In addition, U.S. Patent No. 4,190,608 discloses similarly promoted bismuth-molybdenum-iron catalyst for oxidation of olefins. U.S. Patent Nos. 5,093,299, 5212,137, 5,658,842 and 5, 834,394 are directed to bismuth-molybdenum promoted catalysts exhibiting high yields to acrylonitrile.

An object of the instant invention is a novel catalyst comprising a unique combination of promoters offering better performance in the catalytic ammoxidation of propylene, isobutylene or mixtures thereof, to acrylonitrile, methacrylonitrile and mixtures thereof, respectively.

Summary of the Invention

Disclosed herein is an improved catalyst and process for the ammoxidation of propylene and/or isobutylene to acrylonitrile and/or methacrylonitrile, respectively.

In one aspect, there is provided a catalyst comprising a complex of catalytic oxides comprising rubidium, cerium, chromium, magnesium, iron, bismuth, molybdenum, and at

least one of nickel or nickel and cobalt, wherein the relative ratios of these elements are represented by the following general formula

$$Rb_a Ce_b Cr_c Mg_d A_e Fe_f Bi_g Mo_{12} O_x$$

wherein A is Ni or the combination of Ni and Co,

a is about 0.01 to about 1,

b is about 0.01 to about 3,

c is about 0.01 to about 2,

d is about 0.01 to about 7,

e is about 0.01 to about 10,

f is about 0.01 to about 4,

g is about 0.05 to about 4,

x is a number determined by the valence requirements of the other elements present,

wherein "b" + "c" is greater than "g" and wherein the catalyst is substantially free of manganese, a noble metal or vanadium.

In a second aspect, there is provided a catalyst comprising a complex of catalytic oxides comprising rubidium, cerium, chromium, magnesium, iron, bismuth, molybdenum, and at least one of nickel or nickel and cobalt, and optionally one of phosphorus, antimony, tellurium, sodium, lithium, potassium, cesium, thallium, boron, tungsten, calcium, zinc, a rare earth element, or mixtures thereof, wherein the relative ratios of these elements are represented by the following general formula:

$$Rb_a Ce_b Cr_c Mg_d A_e Fe_f Bi_g Y_h Mo_{12} O_x$$

wherein A is Ni or the combination of Ni and Co,

Y is at least one of P, Sb, Te, Li, Na, K, Cs, Tl, B, Ge,

W, Ca, Zn, a rare earth element, or mixtures thereof,

a is about 0.01 to about 1,

b is about 0.01 to about 3,

c is about 0.01 to about 2,

d is about 0.01 to about 7,

e is about 0.01 to about 10,

f is about 0.01 to about 4,

g is about 0.05 to about 4,

h is 0 to about 3,

x is a number determined by the valence requirements of the other elements present,

wherein "b" + "c" is greater than "g", and wherein the catalyst is substantially free of manganese, a noble metal or vanadium.

In one embodiment, there is disclosed a catalyst comprising a complex of catalytic oxides comprising rubidium, cerium, chromium, iron, bismuth, molybdenum, and at least one of nickel or nickel and cobalt, and optionally one of phosphorus, antimony, tellurium, sodium, lithium, potassium, cesium, thallium, boron, tungsten calcium, wherein the relative ratios of these elements are represented by the following general formula:

$$Rb_a Ce_b Cr_c A_e Fe_f Bi_g Y_h Mo_{12} O_x$$

wherein A is Ni or the combination of Ni and Co,

Y is at least one of P, Sb, Te, Na, Li, K, Cs, Tl, B, Ge, W, Ca, Zn, a rare earth element, or mixtures thereof,

a is about 0.01 to about 1,

b is about 0.01 to about 3,

c is about 0.01 to about 2,

e is about 0.01 to about 10,

f is about 0.01 to about 4,

g is about 0.05 to about 4,

h is 0 to about 3,

x is a number determined by the valence requirements of the other elements present,

wherein "b" + "c" is greater than "g", and wherein the catalyst is substantially free of manganese, a noble metal or vanadium.

In a third aspect, there is provided a process for the conversion of an olefin selected from the group consisting of propylene, isobutylene or mixtures thereof, to acrylonitrile, methacrylonitrile, and mixtures thereof, respectively, by reacting in the vapor phase at an elevated temperature and pressure, said olefin with a molecular oxygen containing gas and ammonia in the presence of a catalyst comprising a complex of catalytic oxides comprising rubidium, cerium, chromium, magnesium, iron, bismuth, molybdenum, and at least one of nickel or nickel and cobalt, and optionally one of phosphorus, antimony, tellurium, sodium, lithium, potassium, cesium, thallium, boron, germanium, tungsten, calcium, zinc, a rare earth element, or mixtures thereof, wherein the relative ratios of these elements are represented by the following general formula: $Rb_a Ce_b Cr_c Mg_d A_e Fe_f Bi_g Y_h Mo_{12} O_x$ wherein A is Ni or the combination of Ni and Co, Y is at least one of P, Sb, Te, Li, Na, K, Cs,Tl, B, Ge, W, Ca, Zn, a rare earth element, or mixtures thereof, a is about 0.01 to about 1, b is about 0.01 to about 3, c is about 0.01 to about 2, d is about 0.01 to about 7, e is about 0.01 to about 10, f is about 0.01 to about 4, g is about 0.05 to about 4, h is 0 to about 3, x is a number determined by the valence requirements of the other elements present, wherein "b" + "c" is greater than g, and wherein the catalyst is substantially free of manganese, a noble metal or vanadium.

Disclosed herein are processes for the conversion of an olefin selected from the group consisting of propylene, isobutylene or mixtures thereof, to acrylonitrile, methacrylonitrile and mixtures thereof, respectively, by reacting in the vapor phase at an elevated temperature and pressure said olefin with a molecular oxygen containing gas and ammonia in the presence of an mixed metal oxide catalyst, wherein the catalyst is as described above.

DETAILED DESCRIPTION OF THE INVENTION

The instant invention is a novel catalyst comprising a unique combination and ratio of promoters offering better performance in the catalytic ammoxidation of propylene, isobutylene or mixtures thereof, to acrylonitrile, methacrylonitrile and mixtures thereof, respectively.

One embodiment of the present invention is directed to an ammoxidation catalyst comprising a complex of catalytic oxides comprising rubidium, cerium, chromium magnesium, iron, bismuth, molybdenum, and at least one of nickel or nickel and cobalt, wherein the relative ratios of these elements are represented by the following general formula:

$$Rb_a Ce_b Cr_c Mg_d A_e Fe_f Bi_g Mo_{12} O_x$$

wherein A is Ni or the combination of Ni and Co,
a is about 0.01 to about 1,
b is about 0.01 to about 3,
c is about 0.01 to about 2,
d is about 0.01 to about 7,
e is about 0.01 to about 10,
f is about 0.01 to about 4,
g is about 0.05 to about 4,
x is a number determined by the valence requirements of the other elements present,

wherein "b" + "c" is greater than "g", and wherein the catalyst is substantially free of manganese, a noble metal or vanadium. In another embodiment, "b" is also greater than "c". In another embodiment of this invention, "a" is 0.05 to 0.3.

In yet another embodiment, the present invention is directed to an ammoxidation catalyst comprising catalyst comprising a complex of catalytic oxides comprising rubidium, cerium, chromium, iron, bismuth, molybdenum, and at least one of nickel or nickel and cobalt, optionally magnesium, and optionally one of phosphorus, antimony, tellurium, sodium, lithium, potassium, cesium, boron, germanium, tungsten and calcium, wherein the relative ratios of these elements are represented by the following general formula:

$$Rb_a Ce_b Cr_c Mg_d A_e Fe_f Bi_g Y_h Mo_{12} O_x$$

wherein A is Ni or the combination of Ni and Co,
Y is at least one of P, Sb, Te, Li, Na, K, Cs, Tl, B, Ge, W,
Ca, Zn, a rare earth element, or mixtures thereof,
a is about 0.01 to about 1,

b is about 0.01 to about 3,

c is about 0.01 to about 2,

d is 0 to about 7, preferably d is about 0.01 to about 7,

e is about 0.01 to about 10,

f is about 0.01 to about 4,

g is about 0.05 to about 4,

h is 0 to about 3,

x is a number determined by the valence requirements of the other elements present,

wherein "b" + "c" is greater than "g", and wherein the catalyst is substantially free of manganese, a noble metal or vanadium. In another embodiment, "b" is also greater than "c". In another embodiment of this invention, "a" is 0.05 to 0.3.

In the above described catalyst compositions, the amount (on an atomic basis) of cerium plus chromium are greater than the amount of bismuth (i.e. "b" + "c" is greater than "g"). If the amount (on an atomic basis) of cerium plus chromium is less than the amount of bismuth, then the catalysts are not as active. In another embodiment, the amount (on an atomic basis) of cerium is greater than the amount of chromium (i.e. "b" is greater than "c").

The basic catalyst composition described herein is a complex of catalytic oxides of rubidium, cerium, chromium, magnesium, iron, bismuth, molybdenum, and at least one of nickel or nickel and cobalt. Except for specifically excluded elements, other elements or promoters may be included. In one embodiment, the catalyst may include one or more of phosphorus, antimony, tellurium, sodium, lithium, potassium, cesium, thallium, boron, germanium, tungsten, calcium, zinc, and a rare earth element (defined herein as any one of La, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, or Yb). In another embodiment, the base catalyst may not contain magnesium. In yet another embodiment, the catalyst contains a small amount of phosphorus, which has a beneficial effect on the attrition resistance of the catalyst.

Additionally, for the conversion of propylene, ammonia and oxygen to acrylonitrile, the inclusion of certain elements have been identified as being detrimental to obtaining a catalyst with improved acrylonitrile yields. These are manganese, the noble metals (as used herein "noble metals" refers to ruthenium, rhodium, palladium, osmium, iridium and platinum) and vanadium. The inclusion of a noble metal in the catalyst promotes the oxidation of ammonia thereby decreasing the amount of ammonia available for acrylonitrile production. The inclusion of vanadium produces a catalyst which is more active in reacting the propylene

feedstock and less selective to the desired products thereby producing more carbon oxides (CO_x) and less acrylonitrile. The inclusion of manganese in the catalyst results in lesser yields of acrylonitrile. As such the catalyst of the instant invention is described as being substantially free of manganese, a noble metal and/or vanadium. As used herein, "substantially free", with respect to manganese and vanadium, means having an atomic ratio with respect to molybdenum of less than 0.2:12. As used herein, "substantially free", with respect to a noble metal means having an atomic ratio with respect to molybdenum of less than 0.005:12. Preferably, the catalysts contain no manganese, noble metals and/or vanadium.

The catalyst of the present invention may be used either supported or unsupported (i.e. the catalyst may comprise a support). Suitable supports are silica, alumina, zirconium, titania, or mixtures thereof. 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. the complex of catalytic oxides described above) and the support is crucial to obtain an acceptable activity and hardness (attrition resistance) for the catalyst. Directionally, any increase in the active phase increases the activity of the catalyst, but decreases the hardness of the 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 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. Support materials are available which may contain one or more promoter elements, e.g. a silica sol containing sodium (Na), and such promoter elements may be incorporated into the catalyst via the support material.

In one embodiment the catalyst is supported using a silica sol. If the average colloidal particle diameter of said silica sol is too small, the surface area of the manufactured catalyst will be increased and the catalyst will exhibit reduced selectivity. If the colloidal particle diameter is too large, the manufactured catalyst will have poor anti-abrasion strength. Typically, the average colloidal particle diameter of the silica sol is between about 15 nm and about 50 nm. In one embodiment of this invention, the average colloidal particle diameter of the silica sol is about 10 nm and can be as low as about 8 nm. In another embodiment of this invention, the average colloidal particle diameter of the silica sol is about 100 nm. In another embodiment of this invention, the average colloidal particle diameter of the silica sol is about 20 nm.

The catalysts of the present invention may be prepared by any of the numerous methods of catalyst preparation which are known to those of skill in the art. For example, the catalyst may be manufactured by co-precipitating the various ingredients. The co-precipitating mass may then be dried and ground to an appropriate size. Alternatively, the co-precipitated material may be slurried and spray dried in accordance with conventional techniques. The catalyst may be extruded as pellets or formed into spears in oil as is well known in the art. For particular procedures for manufacturing the catalyst, see U.S. Patent Nos. 5,093,299; 4,863,891 and 4,766,232, herein incorporated by reference. In one embodiment, the catalyst components may be mixed with a support in the form of the slurry followed by drying or the catalyst components may be impregnated on silica or other supports.

Bismuth may be introduced into the catalyst as an oxide or as a salt, which upon calcination will yield the oxide. The water-soluble salts which are easily dispersed but form stable oxides upon heat-treating are preferred. An especially preferred source for introducing bismuth is bismuth nitrate.

The iron component into the catalyst may be obtained from any compound of iron which, upon calcination will result in the oxides. As with the other elements, water soluble salts are preferred for the ease with which they may be uniformly dispersed within the catalyst. Most preferred is ferric nitrate.

The molybdenum component of the catalyst may be introduced from any molybdenum oxide. However, it is preferred that a hydrolizable or decomposable molybdenum salt be utilized as the source of the molybdenum. The most preferred starting material is ammonium heptamolybdate.

Other required components and optional promoters of the catalyst, (e.g. Ni, Co, Mg, Cr, P, Sn, Te, B, Ge, Zn, In, Ca, W, or mixtures thereof) may be derived from any suitable source. For example, cobalt, nickel and magnesium may be introduced into the catalyst using nitrate salts. Additionally, magnesium may be introduced into the catalyst as an insoluble carbonate or hydroxide which upon heat treating results in an oxide. Phosphorus may be introduced in the catalyst as an alkaline metal salt or alkaline earth metal salt or the ammonium salt but is preferably introduced as phosphoric acid.

Required and optional alkali components of the catalyst (e.g. Rb, Li, Na, K, Cs, Tl, or mixtures thereof) may be introduced into the catalyst as an oxide or as a salt, which upon calcination will yield the oxide. Preferably, salts such as nitrates which are readily available and easily soluble are used as the means of incorporating such elements into the catalyst.

The catalysts are typically prepared by mixing an aqueous solution of ammonium heptamolybdate with a silica sol to which a slurry containing the compounds, preferably nitrates of the other elements, is added. The solid material is then dried, denitrified and calcined. Preferably the catalyst is spray-dried at a temperature of between 110°C to 350°C, preferably 110°C to 250°C, most preferably 110°C to 180°C. The denitrification temperature may range from 100°C to 500°C, preferably 250°C to 450°C. Finally, calcination takes place at a temperature of between 300°C to 700°C, preferably between 350°C to 650°C.

The catalysts of the instant invention are useful in ammoxidation processes for the conversion of an olefin selected from the group consisting of propylene, isobutylene or mixtures thereof, to acrylonitrile, methacrylonitrile and mixtures thereof, respectively, by reacting in the vapor phase at an elevated temperature and pressure said olefin with a molecular oxygen containing gas and ammonia in the presence of the catalyst.

Preferably, the ammoxidation reaction is performed in a fluid bed reactor although other types of reactors such as transport line reactors are envisioned. Fluid bed reactors, for the manufacture of acrylonitrile are well known in the prior art. For example, the reactor design set forth in U.S. Patent No. 3,230,246, herein incorporated by reference, is suitable.

Conditions for the ammoxidation reaction to occur are also well known in the prior art as evidenced by U.S. Patent Nos. 5,093,299; 4,863,891; 4,767,878 and 4,503,001; herein incorporated by reference. Typically, the ammoxidation process is performed by contacting propylene or isobutylene in the presence of ammonia and oxygen with a fluid bed catalyst at an elevated temperature to produce the acrylonitrile or methacrylonitrile. Any source of oxygen may be employed. For economic reasons, however, it is preferred to use air. The typical molar ratio of the oxygen to olefin in the feed should range from 0.5:1 to 4:1, preferably from 1:1 to 3:1.

The molar ratio of ammonia to olefin in the feed in the reaction may vary from between 0.5:1 to 2:1. There is really no upper limit for the ammonia-olefin ratio, but there is generally no reason to exceed a ratio of 2:1 for economic reasons. Suitable feed ratios for use with the catalyst of the instant invention for the production of acrylonitrile from propylene are an ammonia to propylene ratio in the range of 0.9:1 to 1.3:1, and air to propylene ratio of 8.0:1 to 12.0:1. The catalyst of the instant invention provides high yields of acrylonitrile at relatively low ammonia to propylene feed ratios of about 1:1 to about 1.05:1. These "low ammonia conditions" help to reduce unreacted ammonia in the reactor effluent, a condition

known as "ammonia breakthrough", which subsequently helps to reduce process wastes. Specifically, unreacted ammonia must be removed from the reactor effluent prior to the recovery of the acrylonitrile. Unreacted ammonia is typically removed by contacting the reactor effluent with sulfuric acid to yield ammonium sulfate or by contacting the reactor effluent with acrylic acid to yield ammonium acrylate, which in both cases results in a process waste stream to be treated and/or disposed.

The reaction is carried out at a temperature of between the ranges of about 260°C to 600°C, preferred ranges being 310°C to 500°C, especially preferred being 350°C to 480°C. The contact time, although not critical, is generally in the range of 0.1 to 50 seconds, with preference being to a contact time of 1 to 15 seconds.

The products of reaction may be recovered and purified by any of the methods known to those skilled in the art. One such method involves scrubbing the effluent gases from the reactor with cold water or an appropriate solvent to remove the products of the reaction and then purifying the reaction product by distillation.

The primary utility of the catalyst of the instant invention is for the ammoxidation of propylene to acrylonitrile. However, the instant catalyst may also be used for the oxidation of propylene to acrylic acid. Such processes are typically two stage processes, wherein propylene is converted in the presence of a catalyst to primarily acrolein in the first stage and the acrolein is converted in the presence of a catalyst to primarily acrylic acid in the second stage. The catalyst described herein is suitable for use in the first stage for the oxidation of propylene to acrolein.

SPECIFIC EMBODIMENTS

In order to illustrate the instant invention, catalyst of the instant invention as well as similar catalysts omitting one or more of these elements or additionally including elements detrimental to acrylonitrile production, were prepared and then evaluated under similar reaction conditions. These examples are provided for illustrative purposes only.

Catalyst Preparation

Example 1:

A catalyst of the formula 50 wt % $Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Rb_{0.15}Mo_{12}O_{48.4}$+ 50 wt% SiO2 was prepared as follows: The metal nitrates in the following the order, $Fe(NO_3)_3{\cdot}9H_2O$ (69.752g), $Ni(NO_3)_2{\cdot}6H_2O$ (139.458g), $Mg(NO_3)_2{\cdot}6H_2O$ (49.186g), $Bi(NO_3)_3{\cdot}5H_2O$(20.937g), $RbNO_3$(2.122g), and $(NH_4)_2Ce(NO_3)_6$ (94.654g of a 50% solution) were melted together at ~70°C in a 1000 ml beaker. Ammonium heptamolybdate (AHM)(203.219g) was dissolved in

310 ml of distilled water. To this solution CrO_3 (0.959g) dissolved in a 20ml water was added. Then the silica (871.08g of a 28.75% SiO_2 sol) was added followed by the metal nitrates melt. The resulted yellow slurry was then spray dried. The obtained material was denitrified at 290°C/3 hours and 425°C for 3 hours and then was calcined at 570°C for 3 hours, in air.

Example 2:

50 wt% $Ni_{2.5}Mg_{2.0}Co_{2.5}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Rb_{0.15}Mo_{12}O_{48.4}$ + 50 wt% SiO_2

This catalyst was prepared as described in Example 1. The recipe of this catalyst was as follows: $Fe(NO_3)_3 \cdot 9H_2O$ (69.737g), $Ni(NO_3)_2 \cdot 6H_2O$ (69.714g), $Mg(NO_3)_2 \cdot 6H_2O$ (49.176g), $Co(NO_3)_2 \cdot 6H_2O$ (69.774g), $Bi(NO_3)_3 \cdot 5H_2O$ (20.993g), $RbNO_3$(2.121g), and $(NH_4)_2Ce(NO_3)_6$ (94.634g of a 50% solution) were melted together at ~70°C in a 1000 ml beaker. Ammonium heptamolybdate (AHM)(203.175g) was dissolved in 310 ml of distilled water. To this solution CrO_3 (0.959g) dissolved in a 20ml water was added. Then the silica (796.178g of a 31.4% SiO_2 sol) was added followed by the metal nitrates melt.

Example 3:

50 wt% $Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Li_{0.3}Rb_{0.15}Mo_{12}O_{48.55}$ + 50 wt% SiO_2

This catalyst was prepared as described in Example 1. The recipe of this catalyst was as follows: $Fe(NO_3)_3 \cdot 9H_2O$ (69.632g), $Ni(NO_3)_2 \cdot 6H_2O$ (139.219g), $Mg(NO_3)_2 \cdot 6H_2O$ (49.102g), $LiNO_3$ (1.981g), $Bi(NO_3)_3 \cdot 5H_2O$ (20.901g), $RbNO_3$ (2.118g), and $(NH_4)_2Ce(NO_3)_6$ (94.634g of a 50% solution) were melted together at ~70°C in a 1000 ml beaker. Ammonium heptamolybdate (AHM)(202.87g) was dissolved in 310 ml of distilled water. To this solution CrO_3 (0.958g) dissolved in a 20ml water was added. Then the silica (796.178g of a 31.4% SiO_2 sol) was added followed by the metal nitrates melt.

Example 4:

50 wt% $Ni_{2.5}Mg_{2.0}Co_{2.5}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}P_{0.1}W_{0.1}Rb_{0.15}Mo_{12}O_{48.95}$ + 50 wt% SiO_2

This catalyst was prepared as described in Example 1. The recipe of this catalyst was as follows: $Fe(NO_3)_3 \cdot 9H_2O$ (68.936g), $Ni(NO_3)_2 \cdot 6H_2O$ (68.914g), $Mg(NO_3)_2 \cdot 6H_2O$ (48.611g), $Co(NO_3)_2 \cdot 6H_2O$ (68.973g), $Bi(NO_3)_3 \cdot 5H_2O$ (20.693g), $RbNO_3$ (2.097g), and $(NH_4)_2Ce(NO_3)_6$ (93.547g of a 50% solution)were melted together at ~70°C in a 1000 ml beaker. Ammonium heptamolybdate (AHM)(200.842g) was dissolved in 310 ml of distilled water. To this solution, H_3PO_4 (1.093g of a 85% solution), $(NH_4)_6H_2W_{12}O_{40}$ (2.388g), and CrO_3 (0.948g) dissolved in a 20ml water was added. Then the silica (796.178g of a 31.4% SiO_2 sol) was added followed by the metal nitrates melt.

Example 5:

50 wt% $Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Na_{0.2}Rb_{0.15}Mo_{12}O_{48.5}$ + 50 wt% SiO_2

This catalyst was prepared as described in Example 1. The recipe of this catalyst was as follows: $Fe(NO_3)_3 \cdot 9H_2O$ (69.586g), $Ni(NO_3)_2 \cdot 6H_2O$ (139.127g), $Mg(NO_3)_2 \cdot 6H_2O$ (49.07g), $NaNO_3$ (1.626g), $Bi(NO_3)_3 \cdot 5H_2O$ (20.888g), $RbNO_3$ (2.117g), and $(NH_4)_2Ce(NO_3)_6$ (94.429g of a 50% solution) were melted together at ~70°C in a 1000 ml beaker. Ammonium heptamolybdate (AHM)(202.736g) was dissolved in 310 ml of distilled water. To this solution CrO_3 (0.957g) dissolved in a 20ml water was added. Then the silica (796.178g of a 31.4% SiO_2 sol) was added followed by the metal nitrates melt.

Example 6:

50 wt% $Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}P_{0.1}Rb_{0.15}Mo_{12}O_{48.65}$ + 50 wt% SiO_2

This catalyst was prepared as described in Example 1. The recipe of this catalyst was as follows: $Fe(NO_3)_3 \cdot 9H_2O$ (69.562g), $Ni(NO_3)_2 \cdot 6H_2O$ (139.079g), $Mg(NO_3)_2 \cdot 6H_2O$ (49.053g), $Bi(NO_3)_3 \cdot 5H_2O$ (20.881g), $RbNO_3$ (2.097g), and $(NH_4)_2Ce(NO_3)_6$ (94.397g of a 50% solution) were melted together at ~70°C in a 1000 ml beaker. Ammonium heptamolybdate (AHM)(202.667g) was dissolved in 310 ml of distilled water. To this solution H_3PO_4 (1.103g of a 85%solution) and CrO_3 (0.957g) dissolved in a 20ml water was added. Then the silica (796.178g of a 31.4% SiO_2 sol) was added followed by the metal nitrates melt.

Comparative Examples A through D:

A. 50 wt% $Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Rb_{0.15}Mo_{12}O_{48.25}$ + 50 wt% SiO_2

B. 50 wt% $Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Cr_{0.1}Rb_{0.15}Mo_{12}O_{46.6}$ + 50 wt% SiO_2

C. 50 wt% $Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}K_{0.15}Mo_{12}O_{48.4}$ + 50 wt% SiO_2

D. 50 wt% $Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Cs_{0.15}Mo_{12}O_{48.4}$ + 50 wt% SiO_2

Using the preparation described in Example 1 above, several other catalyst were similarly prepared which omitted one or more of chromium, cerium or rubidium from the preparation. In Comparative Examples C and D, cesium ($CsNO_3$, 2.797g) and potassium (KNO_3, 1.458g) was substituted for the rubidium, respectively.

Comparative Example E:

50 wt% $Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Rb_{0.15}Mn_{1.0}Mo_{12}O_{49.4}$ + 50 wt% SiO_2

This catalyst added manganese, $Mn(NO_3)_2$ (32.699g of a 51.1% solution), to the catalyst preparation described in Example 1 above.

Comparative Example F:

50 wt% $Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Rb_{0.15}Pd_{0.1}Mo_{12}O_{48.5}$ + 50 wt% SiO_2

This catalyst added a noble metal, palladium, $Pd(NO_3)_2$ (2.2g) to the catalyst preparation described in Example 1 above.

Comparative Example G:

50 wt% $Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Rb_{0.15}V_{0.5}Mo_{12}O_{49.65}$ + 50 wt% SiO_2

This catalyst added vanadium, NH_4VO_3 (5.514g) to the catalyst preparation described in Example 1 above.

Comparative Example H:

50 wt% $Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.15}Cr_{0.3}Rb_{0.15}Mo_{12}O_{47.2}$ + 50 wt% SiO_2

This catalyst was prepared as described in Example 1. However, on an atomic basis, the molar quantity of cerium plus the molar quantity of chromium equals the molar quantity of bismuth. The recipe of this catalyst is as follows: $Fe(NO_3)_3 \cdot 9H_2O$ (72.939g), $Ni(NO_3)_2 \cdot 6H_2O$ (145.83g), $Mg(NO_3)_2 \cdot 6H_2O$ (51.434g), $Bi(NO_3)_3 \cdot 5H_2O$ (21.894g), $RbNO_3$(2.219g), and $(NH_4)_2Ce(NO_3)_6$ (16.496g of a 50% solution) were melted together at ~70°C in a 1000 ml beaker. Ammonium heptamolybdate (AHM)(212.504g) was dissolved in 310 ml of distilled water. To this solution CrO_3 (3.009g) dissolved in a 20ml water was added. Then the silica (871.08g of a 28.75% SiO_2 sol) was added followed by the metal nitrates melt.

Comparative Examples I:

50 wt % $Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.1}Cr_{0.1}Rb_{0.15}Mo_{12}O_{46.8}$ + 50 wt% SiO_2

This catalyst was prepared as described in Example 1. However, on an atomic basis, the quantity of cerium plus the quantity of chromium is less than the quantity of bismuth. The recipe of this catalyst is as follows: $Fe(NO_3)_3 \cdot 9H_2O$ (73.642g), $Ni(NO_3)_2 \cdot 6H_2O$ (147.236g), $Mg(NO_3)_2 \cdot 6H_2O$ (51.93g), $Bi(NO_3)_3 \cdot 5H_2O$ (22.105g), $RbNO_3$(2.24g), $(NH_4)_2Ce(NO_3)_6$ (11.104g of a 50% solution) were melted together at ~70°C in a 1000 ml beaker. Ammonium heptamolybdate (AHM)(214.553g) was dissolved in 310 ml of distilled water. To this solution CrO_3 (1.013g) dissolved in a 20ml water was added. Then the silica (871.08g of a 28.75% SiO_2 sol) was added followed by the metal nitrates melt.

Comparative Examples J:

50 wt % $Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{2.0}Ce_{0.9}Cr_{0.1}Rb_{0.15}Mo_{12}O_{46.8}$ + 50 wt% SiO_2

This catalyst was prepared as described in Example 1. However, on an atomic basis, the quantity of cerium plus the quantity of chromium is less than the quantity of bismuth. The recipe of this catalyst is as follows: $Fe(NO_3)_3 \cdot 9H_2O$ (61.264g), $Ni(NO_3)_2 \cdot 6H_2O$ (122.488g), $Mg(NO_3)_2 \cdot 6H_2O$ (43.201g), $Bi(NO_3)_3 \cdot 5H_2O$ (81.732g), $RbNO_3$(1.863g), $(NH_4)_2Ce(NO_3)_6$ (83.136g of a 50% solution) were melted together at ~70°C in a 1000 ml beaker. Ammonium

heptamolybdate (AHM)(178.49g) was dissolved in 310 ml of distilled water. To this solution CrO_3 (0.843g) dissolved in a 20ml water was added. Then the silica (871.08g of a 28.75% SiO_2 sol) was added followed by the metal nitrates melt.

Catalyst Testing

All testing was conducted in a 40cc fluid bed reactor. Propylene was feed into the reactor at a rate of 0.06 WWH (i.e. weight of propylene/weight of catalyst/hour). Pressure inside the reactor was maintained at 10 psig. Reaction temperature was 430°C. After a stabilization period of ~20 hours samples of reaction products were collected. Reactor effluent was collected in bubble-type scrubbers containing cold HCl solution. Off-gas rate was measured with soap film meter, and the off-gas composition was determined at the end of the run with the aid of gas chromatograph fitted with a split column gas analyzer. At the end of the recovery run, the entire scrubber liquid was diluted to approximately 200gms with distilled water. A weighted amount of 2-Butanone was used as internal standard in a ~50 grams aliquot of the dilute solution. A 2 µl sample was analyzed in a GC fitted with a flame ionization detector and a Carbowax column. The amount of NH_3 was determined by titrating the free HCl excess with NaOH solution. The following examples are illustrative of our invention.

Table 1

Example	Active Phase Composition	Total $C_3^=$ Conv.	Conv. to AN	Sel. to AN
1	$Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Rb_{0.15}Mo_{12}O_{48.4}$	98.8	80.0	81.0
2	$Ni_{2.5}Mg_{2.0}Co_{2.5}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Rb_{0.15}Mo_{12}O_{48.4}$	99.2	81.8	82.5
3	$Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Li_{0.3}Rb_{0.15}Mo_{12}O_{48.55}$	98.8	79.9	81.4
4	$Ni_{2.5}Mg_{2.0}Co_{2.5}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}P_{0.1}W_{0.1}Rb_{0.15}Mo_{12}O_{48.95}$	99.7	80.9	81.2
5	$Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Na_{0.2}Rb_{0.15}Mo_{12}O_{48.5}$	99.6	81.0	81.3
6	$Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}P_{0.1}Rb_{0.15}Mo_{12}O_{48.65}$	99.6	82.3	82.6
A	$Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Rb_{0.15}Mo_{12}O_{48.25}$	99.4	79.3	79.9
B	$Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Cr_{0.1}Rb_{0.15}Mo_{12}O_{46.6}$	91.2	75.8	83.1
C	$Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}K_{0.15}Mo_{12}O_{48.4}$	99.7	77.6	77.8
D	$Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Cs_{0.15}Mo_{12}O_{48.4}$	96.8	69.6	72.0
E	$Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Rb_{0.15}Mn_{1.0}Mo_{12}O_{49.4}$	97.3	78.0	78.6
F	$Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Rb_{0.15}Pd_{0.1}Mo_{12}O_{48.5}$	99.3	78.7	81.4

Example	Active Phase Composition (Continued)	Total $C_3^=$ Conv.	Conv. to AN	Sel. to AN
G	$Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.9}Cr_{0.1}Rb_{0.15}V_{0.5}Mo_{12}O_{49.65}$	96.4	76.8	79.7
H	$Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.15}Cr_{0.3}Rb_{0.15}Mo_{12}O_{47.2}$	93.5	77.9	83.3
I	$Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{0.45}Ce_{0.1}Cr_{0.1}Rb_{0.15}Mo_{12}O_{46.8}$	94.9	74.4	78.5
J	$Ni_{5.0}Mg_{2.0}Fe_{1.8}Bi_{2.0}Ce_{0.9}Cr_{0.1}Rb_{0.15}Mo_{12}O_{46.8}$	97.7	78.8	80.7

Notes:

1. All test catalyst compositions contained 50% active phase and 50% SiO_2.
2. "Total $C_3^=$ Conv." is the mole percent per pass conversion of propylene to all products.
3. "Conv. to AN" is the mole percent per pass conversion of propylene to acrylonitrile.
4. "Sel. to AN" is the ratio of moles of acrylonitrile produced to moles of propylene converted expressed in percent.

The catalyst composition of the instant invention is unique in that it comprises rubidium, cerium, chromium, magnesium, iron, bismuth, molybdenum, and at least one of nickel or nickel and cobalt, in the substantial absence of manganese, a noble metal or vanadium. This combination of elements in the relative proportions described herein have not previously utilized in a single ammoxidation catalyst formulation. As illustrated in Table 1, for the ammoxidation of propylene to acrylonitrile, a catalyst of the instant invention has exhibited better performance than catalysts comprising similar (but not exact) combinations of elements found in prior art patents. More specifically, catalysts comprising rubidium, cerium, chromium magnesium, iron, bismuth, molybdenum, and at least one of nickel or nickel and cobalt in the substantial absence of manganese, a noble metal or vanadium, exhibited a combination of higher overall conversion of propylene, higher conversions to acrylonitrile, and high selectivity to acrylonitrile compared to similar catalysts falling outside the scope of the instant invention.

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

1. A catalyst composition comprising a complex of catalytic oxides comprising rubidium, cerium, chromium, magnesium, iron, bismuth, molybdenum, and at least one of nickel or nickel and cobalt, wherein the relative ratios of these elements are represented by the following general formula

$$Rb_a\ Ce_b\ Cr_c\ Mg_d\ A_e\ Fe_f\ Bi_g\ Mo_{12}\ O_x$$

wherein A is Ni or the combination of Ni and Co,

a is about 0.01 to about 1,

b is about 0.01 to about 3,

c is about 0.01 to about 2,

d is about 0.01 to about 7,

e is about 0.01 to about 10,

f is about 0.01 to about 4,

g is about 0.05 to about 4,

x is a number determined by the valence requirements of the other elements present,

wherein "b" + "c" is greater than g and wherein the catalyst is substantially free of manganese, a noble metal and vanadium.

2. The catalyst composition of claim 1, wherein b is less than c.

3. The catalyst composition of claim 1 wherein the catalyst comprises phosphorus.

4. The catalyst composition of claim 1 wherein the catalyst comprises at least one of potassium, cesium, sodium, or mixtures thereof.

5. The catalyst composition of claim 1, wherein the catalyst composition comprises a support selected from the group consisting of silica, alumina, zirconium, titania, or mixtures thereof.

6. The catalyst composition of claim 5, wherein the support comprises about 30 and 70 weight percent of the catalyst.

7. The catalyst composition of claim 1, wherein the catalyst composition comprises silica having an average colloidal particle size in between about 8 nm and about 100 nm.

8. A catalyst composition comprising a complex of catalytic oxides comprising rubidium, cerium, chromium, magnesium, iron, bismuth, molybdenum, and at least one of nickel or nickel

and cobalt, and optionally one of phosphorus, antimony, tellurium, sodium, lithium, potassium, cesium, thallium, boron, germanium, tungsten, calcium, zinc, a rare earth element, or mixtures thereof, wherein the relative ratios of these elements are represented by the following general formula:

$$Rb_a\ Ce_b\ Cr_c\ Mg_d\ A_e\ Fe_f\ Bi_g\ Y_h\ Mo_{12}\ O_x$$

wherein A is Ni or the combination of Ni and Co,

Y is at least one of P, Sb, Te, Li, Na, K, Cs,Tl, B, Ge, W,

Ca, Zn, a rare earth element, or mixtures thereof,

a is about 0.01 to about 1,

b is about 0.01 to about 3,

c is about 0.01 to about 2,

d is about 0.01 to about 7,

e is about 0.01 to about 10,

f is about 0.01 to about 4,

g is about 0.05 to about 4,

h is 0 to about 3,

x is a number determined by the valence requirements of the other elements present

wherein "b" + "c" is greater than "g", and wherein the catalyst is substantially free of manganese, a noble metal or vanadium.

9. The catalyst composition of claim 8, wherein b is less than c.

10. The catalyst composition of claim 8, wherein the catalyst comprises phosphorus.

11. The catalyst composition of claim 8, wherein the catalyst comprises at least one of potassium, cesium, sodium, or mixtures thereof.

12. The catalyst composition of claim 8, wherein the catalyst composition comprises a support selected from the group consisting of silica, alumina, zirconium, titania, or mixtures thereof.

13. The catalyst composition of claim 12, wherein the support comprises about 30 to about 70 weight percent of the catalyst.

14. The catalyst composition of claim 8, wherein the catalyst composition comprises silica having an average colloidal particle size in between about 8 nm and about 100 nm.

15. A process for the conversion of an olefin selected from the group consisting of propylene, isobutylene or mixtures thereof, to acrylonitrile, methacrylonitrile, and mixtures thereof, respectively, by reacting in the vapor phase at an elevated temperature and pressure, said olefin with a molecular oxygen containing gas and ammonia in the presence of a catalyst comprising a complex of catalytic oxides comprising rubidium, cerium, chromium, magnesium, iron, bismuth, molybdenum, and at least one of nickel or nickel and cobalt, and optionally one of phosphorus, antimony, tellurium, sodium, lithium, potassium, cesium, thallium, boron, germanium, tungsten, calcium, zinc, a rare earth element, or mixtures thereof, wherein the relative ratios of these elements are represented by the following general formula:

$$Rb_a\ Ce_b\ Cr_c\ Mg_d\ A_e\ Fe_f\ Bi_g\ Y_h\ Mo_{12}\ O_x$$

wherein A is Ni or the combination of Ni and Co,

Y is at least one of P, Sb, Te, Li, Na, K, Cs,Tl, B, Ge, W,

Ca, Zn, a rare earth element, or mixtures thereof,

a is about 0.01 to about 1,

b is about 0.01 to about 3,

c is about 0.01 to about 2,

d is about 0.01 to about 7,

e is about 0.01 to about 10,

f is about 0.01 to about 4,

g is about 0.05 to about 4,

h is 0 to about 3,

x is a number determined by the valence requirements of the other elements present,

wherein "b" + "c" is greater than g, and wherein the catalyst is substantially free of manganese, a noble metal or vanadium.

16. The process of claim 15, wherein b is less than c.

17. The process of claim 15, wherein h is 0.

18. The process of claim 15, wherein the catalyst comprises phosphorus.

19. The process of claim 15, wherein the catalyst comprises at least one of potassium, cesium, sodium, or mixtures thereof.

20. The process of claim 15, wherein the catalyst composition comprises a support selected from the group consisting of silica, alumina, zirconium, titania, or mixtures thereof.

21. The process of claim 20, wherein the support comprises between 30 and 70 weight percent of the catalyst.

22. The process of claim 15, wherein the catalyst composition comprises silica having an average colloidal particle size in between about 8 nm and about 100 nm.