

Description

BACKGROUND OF THE INVENTION

5 This invention relates to an improved process and catalyst for the ammoxidation of olefin-ammonia mixtures to unsaturated nitriles, and more particularly to an improved process and catalyst for the ammoxidation of propylene-ammonia and isobutylene-ammonia to acrylonitrile and methacrylonitrile, respectively. The ammoxidation is conducted in the presence of a catalyst comprising at least one element selected from the group comprising potassium and cesium, and the oxides of bismuth, molybdenum, iron, 10 nickel, and magnesium, and optionally in combination with at least one element selected from the group of cobalt, phosphorus, manganese, tellurium, sodium, cerium, chromium, antimony and tungsten.

There are many patents related to the production of acrylonitrile by use of bismuth-molybdenum-iron fluidized bed catalyst (e.g., 3,642,930). In particular, US-A-4,863,891, issued September 5, 1989, and US-A-4,767,878, issued August 30, 1988, disclose a process for acrylonitrile production using a catalyst 15 comprised of the oxides bismuth, molybdenum, iron, magnesium and optionally the oxides of cobalt, nickel, phosphorous, arsenic and an alkali metal present in an amount less than 0.1. DE-A-2 258 821 also discloses a process for acrylonitrile production using a mixed oxide catalyst comprising these oxides. It does not disclose a catalyst in which Magnesium oxide is combined with an oxide of potassium and/or caesium. DE-A-2 366 002 discloses a process for acrylonitrile production using a mixed oxide catalyst comprising some 20 of these oxides but excluding magnesium oxide.

The catalyst employed in the process of this invention has high activity for the production of unsaturated nitriles at a slightly lower reaction temperature than is normally employed for this type of process, and continues efficient low temperature operation after aging. In addition to high activity for nitrile production, the catalyst has a number of other important advantages that contribute greatly to the efficient 25 and economic operation of the process. The catalyst has excellent redox stability under the reaction conditions of the process. This permits the use of low process air to olefin ratios and high weight hourly space velocities. The catalyst exhibits efficient ammonia utilization thus greatly reducing the amount of unreacted ammonia appearing in the reactor effluent and thus lowering the amount of sulfuric acid required to neutralize the ammonia in the effluent. This results in improvements in (1) the operation of the recovery 30 section of the process and (2) pollution control. The use of lower operating temperatures favors longer catalyst life and minimizes effluent problems such as afterburning. Despite the lower reaction temperatures, per pass conversions to the nitrile product of 84 percent and above are obtained. A further important advantage associated with the catalyst of this invention is the low cost of the essential catalytic components and the ease of catalyst preparation.

35 The reactants employed in producing the unsaturated nitriles of this invention are oxygen, ammonia, and an olefin having three carbon atoms in a straight chain such as propylene or isobutylene, and mixtures thereof.

The olefins may be in a mixture with paraffinic hydrocarbons, such as ethane, propane, butane and pentane; for example, a propylene-propane mixture may constitute the feed. This makes it possible to use 40 ordinary refinery streams without special separation. Likewise, diluents such as nitrogen and oxides of carbon may be present in the reaction mixture without deleterious effect.

In its preferred aspect, the process comprises contacting a mixture comprising propylene or isobutylene, ammonia and oxygen with the catalyst at an elevated temperature and at atmospheric or near atmospheric pressure to produce acrylonitrile or methacrylonitrile. Most preferably, the process is directed 45 to contacting propylene, ammonia and oxygen with a fluid bed catalyst at an elevated temperature to produce acrylonitrile.

Any sources of oxygen may be employed in this process. For economic reasons, however, it is preferred that air be employed as the source of oxygen. From a purely technical viewpoint, relatively pure molecular oxygen will give equivalent results. The molar ratio of oxygen to the olefin in the feed to the 50 reaction vessel should be in the range of 0.5:1 to 4:1 and a ratio of about 1:1 to 3:1 is preferred.

The molar ratio of ammonia to olefin in the feed to the reaction may vary between about 0.5:1 to 5:1. There is no real upper limit for the ammonia-olefin ratio, but there is generally no reason to exceed a ratio of 5:1. At ammonia-olefin ratios appreciably less than the stoichiometric ratio of 1:1, various amounts of oxygenated derivatives of the olefin will be formed. Outside the upper limit of this range only insignificant 55 amounts of aldehydes and acids will be produced, and only very small amounts of nitriles will be produced at ammonia-olefin ratios below the lower limit of this range. It is surprising that within the ammonia-olefin range stated, maximum utilization of ammonia is obtained, and this is highly desirable. It is generally possible to recycle any unreacted olefin and unconverted ammonia.

We have found that in some cases water in the mixture fed to the reaction vessel improves the selectivity of the reaction and yield of nitrile. However, addition of water to the feed is not essential in this invention, inasmuch as water is formed in the course of the reaction.

In general, the molar ratio of added water to olefin, when water is added, is above about 0.25:1. Ratios on the order of 1:1 to 4:1 are particularly desirable, but higher ratios may be employed, i.e., up to about 10:1.

The reaction is carried out at a temperature within the range of from about 260° to about 600°C. The preferred temperature range is from about 310° to 500°C, especially preferred being from about 315° to 480°C.

The pressure at which the reaction is conducted is another variable, and the reaction is preferably carried out at about atmospheric or above atmospheric 200 to 500 KPa (2 to 5 atmospheres) pressure.

The apparent contact time is not critical, and contact times in the range of from 0.1 to about 50 seconds may be employed. The optimum contact time will, of course, vary depending upon the olefin being reacted, but in general, a contact time of from 1 to 15 seconds is preferred.

Generally any apparatus of the type suitable for carrying out oxidation/ammoxidation reactions in the vapor phase may be employed in the execution of this process. The process may be conducted either continuously or intermittently. The catalyst bed may be a fixed-bed employing a large particulate or pelleted catalyst or preferably, a so-called "fluidized" bed of catalyst may be employed. Any conventional fluid ammoxidation reactor may be utilized in the practice of the process of the present invention. For example, the reactor described in US-A-3,230,246, issued January 18, 1966 incorporated herein by reference would be suitable in the practice of the present invention.

The reactor may be brought to the reaction temperature before or after the introduction of the reaction feed mixture. However, in a large scale operation it is preferred to carry out the process in a continuous manner, and in such a system the circulation of the unreacted olefin is contemplated. Periodic regeneration or reactivation of the catalyst is also contemplated, and this may be accomplished, for example, by contacting the catalyst with air at an elevated temperature.

The products of the reaction may be recovered 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. If desired, acidified water can be used to absorb the products of reaction and neutralize unconverted ammonia. The ultimate recovery of the products may be accomplished by conventional means. The efficiency of the scrubbing operation may be improved when water is employed as the scrubbing agent by adding a suitable wetting agent in the water. Where molecular oxygen is employed as the oxidizing agent in this process, the resulting product mixture after the removal of the nitriles may be treated to remove carbon dioxide, with the remainder of the mixture containing the unreacted olefin and oxygen being recycled through the reactor. In the case where air is employed as the oxidizing agent in lieu of molecular oxygen, the residual product after separation of the nitriles and other carbonyl products may be scrubbed with a non-polar solvent, e.g., a hydrocarbon fraction in order to recover unreacted olefin, and in this case the remaining gases may be discarded. The addition of a suitable inhibitor to prevent polymerization of the unsaturated products during the recovery steps is also contemplated.

The catalyst useful in the process of the present invention is a mixture, compound or possibly complex of the oxides of iron, bismuth, molybdenum, nickel and magnesium, at least one or more element selected from potassium and cesium, and optionally one or more elements selected from the group comprising cobalt, manganese, chromium, phosphorous, antimony, tellurium, sodium, cerium and/or tungsten. The composition is characterized by in the following empirical formula:



wherein A is one or more of the elements selected from the group comprising cobalt, manganese, chromium, phosphorus, antimony, tellurium, sodium, cerium and tungsten wherein (a) is a number from 0 to less than 5, (b) is a number from 0 to 0.4, (c) is a number from 0 to 0.4, provided that the sum of (b) and (c) is from 0.1 to 0.4, (d), (e), (f), and (g) are a number from about 0.2 to 10, and (x) is a number determined by the valence requirements of the other elements present. Preferably, the sum of (b) and (c) is a number from greater than 0.1 to 0.4. More preferably the sum of (b) and (c) is a number from 0.125-0.3.

The catalyst of this invention may be prepared by any of the numerous methods of catalyst preparation which are known to those skilled in the art. For example, the catalyst may be manufactured by co-precipitating the various ingredients. The co-precipitated 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 spheres in oil as is well-known in the art. Alternatively, the catalyst components may be mixed with the support in the form of the slurry followed by drying, or they may be impregnated on silica or other supports.

A particularly attrition-resistant form of the catalyst may be prepared by adding the support material to the catalyst in two stages, first by preparing and heat-treating a mixture of active catalyst components and from 0 to 60% by weight of the total support material, followed by adding the remainder of the support material to the powdered form of the heat-treated catalyst.

Potassium, cesium, and sodium may be introduced into the catalyst as an oxide or as any salt which upon calcination will yield the oxide. Preferred salts are the nitrates which are readily available and easily soluble.

Bismuth may be introduced into the catalyst as an oxide or as any salt which upon calcination will yield the oxide. Preferred are the water-soluble salts which are easily dispersible within the catalyst and which form stable oxides upon heat-treating. An especially preferred source for introducing bismuth is bismuth nitrate which has been dissolved in a dilute solution of HNO_3 .

To introduce the iron component into the catalyst one may use 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. Cobalt, nickel and magnesium may be similarly introduced. However, magnesium may also be introduced into the catalyst as an insoluble carbonate or hydroxide which upon heat-treating results in an oxide.

To introduce the molybdenum component, any molybdenum oxide such as the dioxide, trioxide, pentoxide, or sesquioxide may be used; more preferred is a hydrolyzable or decomposable molybdenum salt. The most preferred starting material is ammonium heptamolybdate.

Phosphorus may be introduced as an alkali metal salt, an alkaline earth metal salt or the ammonium salt, but is preferably introduced as phosphoric acid.

Other elements may be introduced, starting with the metal, oxidizing the metal with an oxidizing acid such as nitric acid, and then incorporating the nitrate into the catalyst. Generally, however, the nitrates are readily available and form a very convenient starting material.

Other variations in starting materials will suggest themselves to one skilled in the art, particularly when the preferred starting materials mentioned hereinabove are unsuited to the economics of large-scale manufacture. In general, any compounds containing the desired catalyst components may be used provided that they result in the oxides of the instant catalyst upon heating to a temperature within the range disclosed hereinafter.

The catalyst can be employed without a support and will display excellent activity. The catalyst can also be combined with a support, and preferably it is combined with at least 10 percent up to about 90 percent of the supporting compound by weight of the entire composition. Any known support materials can be used, such as, silica, alumina, zirconia, titania, alundum, silicon carbide, alumina-silica, the inorganic phosphates such as aluminum phosphate, silicates, aluminates, borates, carbonates, and materials such as pumice, montmorillonite, and the like that are stable under the reaction conditions to be encountered in the use of the catalyst. The preferred support is silica, which is added to the slurry during the preparation of the catalyst in the form of silica sol or fumed silica. The level of support is usually in the range of 10-70% weight present. Preferably, the level of support is in the range of 40-60% weight present.

The catalytic activity of the system is enhanced by heating at an elevated temperature. Generally, the catalyst mixture is spray dried at a temperature of between about 110°C to 350°C and then heat treated in stages for from about one to twenty-four hours or more at a temperature of from about 260° to about 1000°C , preferably from $300\text{--}400^\circ\text{C}$ to $550\text{--}700^\circ\text{C}$.

In general, activation of the catalyst is achieved in less time at higher temperatures. The sufficiency of activation at any given set of conditions is ascertained by a spot test of a sample of the material for catalytic activity. Activation is best carried out in an open chamber, permitting circulation of air or oxygen, so that any oxygen consumed can be replaced.

Further, pre-treatment or activation of the catalyst before use with a reducing agent such as ammonia in the presence of a limited amount of air at a temperature in the range of 260° to 540°C is also beneficial.

A preferred method of preparing the catalyst of this invention and a more complete description of the process of the invention can be obtained from the following examples. In addition to the production of unsaturated nitriles, the catalyst of this invention is also useful for the conversion of olefins, such as propylene and isobutylene, to the corresponding unsaturated aldehydes and unsaturated carboxylic acids.

EXAMPLES 1 TO 10

The catalysts employed in the examples of this invention were prepared by essentially the same procedure as described herein below, using the appropriate starting materials.

5 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in H_2O on a hot plate. The other nitrates were then added in the following order; $\text{Mn}(\text{NO}_3)_2$ -50% Soln., $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, KNO_3 -10% Soln., and CsNO_3 -10% Soln. A dark greenish brown solution was formed which was maintained at approximately 60°C . $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was dissolved in H_2O , at approximately 60°C . A silica sol (a highly dispersed colloidal silica) was added, followed by addition of CrO_3 (which had been dissolved in H_2O). Next, the
10 nitrate solution was added to form a greenish yellow slurry, which was then evaporated on a hot plate with constant stirring until thickening occurred. The next step involved drying at about 120°C . Following drying, the catalyst was denitrified by heating at 290°C for 3 hours, followed by heating at 425°C for 3 hours, and finally calcining at about 610°C for 3 hours. Table I shows the starting materials for each example catalyst prepared by the above described procedure.

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TABLE I
STARTING MATERIALS FOR CATALYST FORMATION (Grams)

Example	KNO ₃	C ² NO ₃	Ni(NO ₃) ₂ ·6H ₂ O	NaNO ₂	Hg(NO ₃) ₂ ·6H ₂ O	Co(NO ₃) ₂ ·6H ₂ O	Pb(NO ₃) ₂ ·9H ₂ O	Mn(NO ₃) ₂ ·5H ₂ O	Bi(NO ₃) ₃ ·5H ₂ O	H ₃ PO ₄ 85% soln	WO ₃ 85% soln	CrO ₃	(NH ₄) ₆ Mo ₇ O ₂₄	SiO ₂ Sol -40%
1	*0.61	*0.88	21.81	—	7.69	—	10.91	2.42	3.27	—	—	0.68	31.78	93.29
2	*1.36	*2.05	21.81	—	7.69	—	10.91	2.42	3.27	—	—	0.68	31.78	93.59
3	0.61	0.88	21.81	—	7.69	—	10.91	2.42	3.27	—	—	0.68	31.78	95.36
4	*0.30	*0.29	17.45	—	9.62	2.18	12.12	—	3.64	—	2.05	—	31.78	95.36
5	*2.27	*1.46	17.45	—	9.62	2.18	12.12	—	3.64	—	2.05	—	31.78	95.80
6	0.76	1.46	17.45	—	9.62	2.18	12.12	—	3.64	—	2.05	—	31.78	98.79
7	*0.45	—	21.81	0.64	7.69	—	15.15	—	5.46	0.86	—	—	31.78	97.06
8	*3.79	—	21.81	0.64	7.69	—	15.15	—	5.46	0.86	—	—	31.78	97.45
9	*3.03	*0.44	21.81	0.64	7.69	—	15.15	—	5.46	0.86	—	—	31.78	97.44
10	1.14	*2.92	21.81	0.64	7.69	—	15.15	—	5.46	0.86	—	—	31.78	98.86

* = 10% Solution.

In the examples given, percent conversion to the unsaturated nitrile is defined as follows:

Mole percent per pass conversion (PPC) to unsaturated nitrile =

$$\frac{\text{Mols of nitrile product obtained}}{\text{Total Mols of olefin converted to all products}} \times 100$$

Ammonoxidation reactions carried out with the catalyst compositions of this invention employing propylene as the hydrocarbon feeds are summarized in Table II. Each reaction was run in a 0.95 cm (3/8 inch) diameter stainless steel microreactor. A 3.7 gram sample of 20-35 mesh catalyst was employed. The data in these tables show that per pass conversions to acrylonitrile obtained with catalysts of the present invention are substantially higher than those obtained with catalysts of the prior art.

TABLE II
CONVERSION OF PROPYLENE TO ACRYLONITRILE

Fixed - Bed Reactor

Reaction Temperature: 430°C

Contact Time: 6.0 seconds

Run Time: 30 minutes

Feed Ratio (Molar) $C_3H_6/NH_3/O_2/N_2/H_2O = 1.8/2.2/3.6/2.4/6$

Example	Catalyst Composition	C_3H_6 Conversion	Acrylonitrile % Yield	% Selectivity
* 1. 50%	K _{0.04} Cs _{0.03} Ni ₅ Mg ₂ Fe _{1.8} Mn _{0.45} Bi _{0.45} Cr _{0.45} Mo ₁₂ O _x +50% SiO ₂	100.0	78.6	78.6
2. 50%	K _{0.09} Cs _{0.07} Ni ₅ Mg ₂ Fe _{1.8} Mn _{0.45} Bi _{0.45} Cr _{0.45} Mo ₁₂ O _x +50% SiO ₂	98.8	84.2	85.2
* 3. 50%	K _{0.4} Cs _{0.3} Ni ₅ Mg ₂ Fe _{1.8} Mn _{0.45} Bi _{0.45} Cr _{0.45} Mo ₁₂ O _x +50% SiO ₂	19.4	15.2	78.5
* 4. 50%	K _{0.02} Cs _{0.01} Ni ₄ Co _{0.5} Mg _{2.5} Fe ₂ Bi _{0.5} W _{0.5} Mo ₁₂ O _x +50% SiO ₂	99.1	73.9	74.5
5. 50%	K _{0.15} Cs _{0.05} Ni ₄ Co _{0.5} Mg _{2.5} Fe ₂ Bi _{0.5} W _{0.5} Mo ₁₂ O _x +50% SiO ₂	94.0	80.3	85.4
* 6. 50%	K _{0.50} Cs _{0.50} Ni ₄ Co _{0.5} Mg _{2.5} Fe ₂ Bi _{0.5} W _{0.5} Mo ₁₂ O _x +50% SiO ₂	22.7	17.0	75.0
* 7. 50%	K _{0.03} Na _{0.5} Ni ₅ Mg ₂ Fe _{2.5} Bi _{0.75} P _{0.5} Mo ₁₂ O _x +50% SiO ₂	95.3	69.5	72.6
8. 50%	K _{0.25} Na _{0.5} Ni ₅ Mg ₂ Fe _{2.5} Bi _{0.75} P _{0.5} Mo ₁₂ O _x +50% SiO ₂	95.3	72.8	76.4
9. 50%	K _{0.20} Cs _{0.015} Na _{0.5} Ni ₅ Mg ₂ Fe _{2.5} Bi _{0.75} P _{0.5} Mo ₁₂ O _x +50% SiO ₂	94.9	72.8	76.7
* 10. 50%	K _{0.75} Cs _{0.1} Na _{0.5} Ni ₅ Mg ₂ Fe _{2.5} Bi _{0.75} P _{0.5} Mo ₁₂ O _x +50% SiO ₂	47.3	35.2	74.4

* --- Comparative examples

Claims

1. A process for converting an olefin selected from propylene, isobutylene or mixtures thereof into acrylonitrile, methacrylonitrile or mixtures thereof which comprises reacting the olefin with a molecular



TABLE II
CONVERSION OF PROPYLENE TO ACRYLONITRILE

Fixed - Bed Reactor
Reaction Temperature: 430°C
Contact Time: 6.0 seconds
Run Time: 30 minutes
Feed Ratio (Molar) $C_3=NH_3/O_2/N_2/H_2O = 1.8/2.2/3.6/2.4/6$

Example	Catalyst Composition	C_3 Conversion	Acrylonitrile % Yield	Acrylonitrile % Selectivity
* 1. 50%	K _{0.04} Cs _{0.03} Ni ₁₅ Mg ₂ Fe _{1.8} Mn _{0.45} Bi _{0.45} Cr _{0.45} Mo _{120x} +50% SiO ₂	100.0	78.6	78.6
2. 50%	K _{0.09} Cs _{0.07} Ni ₁₅ Mg ₂ Fe _{1.8} Mn _{0.45} Bi _{0.45} Cr _{0.45} Mo _{120x} +50% SiO ₂	98.8	84.2	85.2
* 3. 50%	K _{0.4} Cs _{0.3} Ni ₅ Mg ₂ Fe _{1.8} Mn _{0.45} Bi _{0.45} Cr _{0.45} Mo _{120x} +50% SiO ₂	19.4	15.2	78.5
* 4. 50%	K _{0.02} Cs _{0.01} Ni ₄ Co _{0.5} Mg _{2.5} Fe ₂ Bi _{0.5} Mo _{120x} +50% SiO ₂	99.1	73.9	74.5
5. 50%	K _{0.15} Cs _{0.05} Ni ₄ Co _{0.5} Mg _{2.5} Fe ₂ Bi _{0.5} Mo _{120x} +50% SiO ₂	94.0	80.3	85.4
* 6. 50%	K _{0.50} Cs _{0.50} Ni ₄ Co _{0.5} Mg _{2.5} Fe ₂ Bi _{0.5} Mo _{120x} +50% SiO ₂	22.7	17.0	75.0
* 7. 50%	K _{0.03} Na _{0.5} Ni ₅ Mg ₂ Fe _{2.5} Bi _{0.75} Po _{0.5} Mo _{120x} +50% SiO ₂	95.3	69.5	72.6
8. 50%	K _{0.25} Na _{0.5} Ni ₅ Mg ₂ Fe _{2.5} Bi _{0.75} Po _{0.5} Mo _{120x} +50% SiO ₂	95.3	72.8	76.4
9. 50%	K _{0.20} Cs _{0.015} Na _{0.5} Ni ₅ Mg ₂ Fe _{2.5} Bi _{0.75} Po _{0.5} Mo _{120x} +50% SiO ₂	94.9	72.8	76.7
* 10. 50%	K _{0.75} Cs _{0.1} Na _{0.5} Ni ₅ Mg ₂ Fe _{2.5} Bi _{0.75} Po _{0.5} Mo _{120x} +50% SiO ₂	47.3	35.2	74.4

* --- Comparative examples

Claims

1. A process for converting an olefin selected from propylene, isobutylene or mixtures thereof into acrylonitrile, methacrylonitrile or mixtures thereof which comprises reacting the olefin with a molecular



oxygen containing gas and ammonia in the vapour phase at a temperature of from about 260°C to 600°C in the presence of an oxide catalyst characterised in that the oxide catalyst has the empirical formula:



wherein

A is Co, Mn, Cr, P, Sb, Te, Na, Ce, W or mixtures thereof; and

10 wherein

a is a number from 0 to 5;

b is a number from 0 to 0.4;

c is a number from 0 to 0.4;

provided that the sum of b and c

15 is from 0.1 to 0.4;

d, e, f, and g are numbers from about 0.2 to 10; and

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

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2. A process as claimed in claim 1 characterised in that the oxide catalyst is one where the sum of b and c is from 0.125 to 0.3.

3. A process as claimed in either claim 1 or claim 2 characterised in that the oxide catalyst is supported on a catalyst support material selected from silica, alumina, zirconia, titania, alundum, silicon carbide, alumina-silica, inorganic phosphates, silicates, aluminates, borates and carbonates, pumice, montmorillonite, or mixtures thereof.

4. A process as claimed in claim 3 characterized in that the catalyst support material is silica.

5. A process as claimed in either claim 3 or claim 4 characterised in that the catalyst support material comprises 40-60% by weight of the oxide catalyst.

6. A process as claimed in any one of claims 1 to 5 characterised in that the olefin is either propylene or isobutylene.

7. A process as claimed in any one of claims 1 to 6 characterised in that the molar ratios of olefin : molecular oxygen containing gas : ammonia are within the ranges 1 : 0.5 to 4 : 0.5 to 5.

8. A process as claimed in any one of claims 1 to 7 characterised by being carried out in a fluid-bed reactor in the presence of steam.

9. A catalyst composition comprising a mixture, compound or complex of the oxides iron, bismuth, molybdenum, nickel and magnesium, at least one or more elements selected from potassium and caesium and optionally one or more elements selected from the group comprising cobalt, manganese, chromium, phosphorous, antimony, tellurium, sodium, cerium and/or tungsten having the empirical formula:



wherein

A is one or more of Co, Mn, Cr, P, Sb, Te, Na, Ce, or W

wherein

a is a number from 0 to less than 5.0;

55 b is a number from 0 to 0.4;

c is a number from 0 to 0.4;

provided that the sum of

b and c is from 0.1 to 0.4;



d, e, f and g are numbers from 0.2 to 10;
and

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

- 5 10. A catalyst composition as claimed in claim 9 characterised in that the sum of b and c is from 0.125 to 0.3.

Patentansprüche

- 10 1. Verfahren zur Umwandlung eines Olefins, ausgewählt aus Propylen, Isobutylen oder Mischungen derselben, zu Acrylnitril, Methacrylnitril oder Mischungen daraus, welches das Umsetzen des Olefins mit einem molekularen Sauerstoff enthaltenden Gas und Ammoniak in der Dampfphase bei einer Temperatur im Bereich von etwa 260 °C bis 600 °C in Gegenwart eines Oxidkatalysators umfaßt, **dadurch gekennzeichnet**, daß der Oxidkatalysator die empirische Formel:



aufweist, worin

A Co, Mn, Cr, P, Sb, Te, Na, Ce, W oder

20 Mischungen daraus bedeutet, und

worin

a eine Zahl von 0 bis 5 ist,

b eine Zahl von 0 bis 0,4 ist,

c eine Zahl von 0 bis 0,4 ist,

- 25 vorausgesetzt, daß die Summe von b und c

im Bereich von 0,1 bis 0,4 liegt,

d, e, f und g Zahlen mit einem Wert von

etwa 0,2 bis 10 sind, und

x eine Zahl ist, die durch die Wertigkeitsanforderungen der anderen vorhandenen Elemente bestimmt wird.

- 30 2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, daß der Oxidkatalysator ein solcher ist, worin die Summe von b und c im Bereich von 0,125 bis 0,3 liegt.
- 35 3. Verfahren nach einem der Ansprüche 1 oder 2, **dadurch gekennzeichnet**, daß der Oxidkatalysator auf einem Katalysator-Trägermaterial geträgert ist, ausgewählt aus Kieselerde, Tonerde, Zirkonerde, Titanerde, Alundum, Siliciumcarbid, Tonerde-Kieselerde, anorganischen Phosphaten, Silicaten, Aluminaten, Boraten und Carbonaten, Bimsstein, Montmorillonit oder Mischungen derselben.
- 40 4. Verfahren nach Anspruch 3, **dadurch gekennzeichnet**, daß das Katalysator-Trägermaterial Kieselerde ist.
5. Verfahren nach einem der Ansprüche 3 oder 4, **dadurch gekennzeichnet**, daß das Katalysator-Trägermaterial 40 bis 60 Gewichtsprozent des Oxidkatalysators umfaßt.
- 45 6. Verfahren nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet**, daß das Olefin entweder Propylen oder Isobutylen ist.
7. Verfahren nach einem der Ansprüche 1 bis 6, **dadurch gekennzeichnet**, daß die molaren Verhältnisse von Olefin : molekularen Sauerstoff enthaltendem Gas : Ammoniak innerhalb der Bereiche 1 : 0,5 bis 4 : 0,5 bis 5 liegen.
- 50 8. Verfahren nach einem der Ansprüche 1 bis 7, **dadurch gekennzeichnet**, daß es in einem Fließbettreaktor in Gegenwart von Dampf durchgeführt wird.
- 55 9. Katalysator-Zusammensetzung, enthaltend eine Mischung, eine Verbindung oder einen Komplex der Oxide von Eisen, Bismut, Molybdän, Nickel und Magnesium, zumindest eines oder mehrere Elemente, ausgewählt aus Kalium und Cäsium, und gegebenenfalls eines oder mehrere Elemente, ausgewählt aus



der Gruppe umfassend Cobalt, Mangan, Chrom, Phosphor, Antimon, Tellur, Natrium, Cer und/oder Wolfram, mit der empirischen Formel:



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worin

A eines oder mehrere der Elemente Co, Mn, Cr, P, Sb, Te, Na, Ce oder W ist,

worin

a eine Zahl von 0 bis weniger als 5,0 bedeutet,

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b eine Zahl von 0 bis 0,4 ist,

c eine Zahl von 0 bis 0,4 ist,

vorausgesetzt, daß die Summe von b und c im Bereich von 0,1 bis 0,4 liegt,

d, e, f und g Zahlen von 0,2 bis 10 bedeuten,

und

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x eine Zahl ist, bestimmt durch die Valenzanforderungen der anderen vorhandenen Elemente.

10. Katalysator-Zusammensetzung nach Anspruch 9, dadurch gekennzeichnet, daß die Summe von b und c im Bereich von 0,125 bis 0,3 liegt.

20 Revendications

1. Un procédé pour la conversion d'une oléfine sélectionnée à partir de propylène, d'isobutylène ou de mélanges de ces deux corps en acrylonitrile, méthacrylonitrile ou des mélanges de ces deux corps, procédé consistant à faire réagir l'oléfine avec un gaz contenant de l'oxygène moléculaire et de l'ammoniac en phase vapeur à une température comprise entre 260 et 600 °C en présence d'un catalyseur type oxyde caractérisé par la formule empirique suivante :

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avec

- A étant du Co, Mn, Cr, P, Sb, Te, Na, Ce, W ou un mélange de ces éléments;
- a étant un nombre compris entre 0 et 5;
- b étant un nombre compris entre 0 et 0,4;
- c étant un nombre compris entre 0 et 0,4, pourvu que la somme b + c soit comprise entre 0,1 et 0,4;
- d, e, f et g étant des nombres compris entre 0,2 et 10, et
- x étant un nombre déterminé par les besoins au point de vue valence des autres éléments présents.

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2. Un procédé selon la revendication 1 caractérisé par le fait que le catalyseur type oxyde est tel que la somme b + c est comprise entre 0,125 et 0,3.

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3. Un procédé selon soit la revendication 1, soit la revendication 2 caractérisé par le fait que ce catalyseur oxyde repose sur un matériau support sélectionné à partir de silice, d'alumine, de zircone, de dioxyde de titane, d'alundon, de carbure de silicium, d'alumine-silice, de phosphates inorganiques, de silicates, d'aluminates, de borates et de carbonates, de pierre ponce, de montmorillonite ou de mélanges de ces corps.

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4. Un procédé selon la revendication 3 caractérisé par le fait que le matériau du support du catalyseur est de la silice.

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5. Un procédé selon soit la revendication 3, soit la revendication 4 caractérisé par le fait que 40 à 60 % du poids du matériau support de catalyseur est constitué du catalyseur oxyde.

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6. Un procédé selon n'importe laquelle des revendications 1 à 5 caractérisé par le fait que l'oléfine est soit du propylène, soit de l'isobutylène.



7. Un procédé selon n'importe laquelle des revendications 1 à 6 caractérisé par le fait que les rapports molaires oléfine/gaz contenant de l'oxygène moléculaire/ammoniac sont dans les gammes 1/0,5 à 4/0,5 à 5.

5 8. Un procédé selon n'importe laquelle des revendications 1 à 7 caractérisé par le fait qu'il a lieu dans un réacteur à lit fluidisé en présence de vapeur.

10 9. Un composé catalytique constitué d'un mélange, d'un composé à base de ou d'un complexe d'oxydes de fer, de bismuth, de molybdène, de nickel et de magnésium, d'au moins un élément ou plus de la paire potassium/césium et facultativement d'un ou plusieurs éléments sélectionnés dans un groupe comprenant cobalt, manganèse, chrome, phosphore, antimoine, tellure, sodium, cérium et/ou tungstène, ayant la formule empirique suivante :



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avec

- A étant un ou plusieurs des éléments Co, Mn, Cr, P, Sb, Te, Na, Ce, W;
- a étant un nombre compris entre 0 et moins de 5,0;
- b étant un nombre compris entre 0 et 0,4;
- c étant un nombre compris entre 0 et 0,4, pourvu que la somme b + c soit comprise entre 0,1 et 0,4;
- d, e, f et g étant des nombres compris entre 0,2 et 10, et
- x étant un nombre déterminé par les besoins au point de vue valence des autres éléments présents.

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10. Un composé catalytique selon la revendication 9 caractérisé par le fait que la somme b + c est comprise entre 0,125 et 0,3.

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