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SPECIFICATION

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PARAFFIN AMMOXIDATION USING VANADIUM ANTIMONY OXIDE
BASED CATALYSTS WITH HALIDE PROMOTERS

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BACKGROUND OF THE INVENTION

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Field of the Invention

The invention relates to an improved process for the catalytic ammoxidation of paraffins containing from 3 to 5 carbon atoms to α,β -unsaturated mono-nitriles, especially paraffins containing 3 to 4 carbon atoms. In particular, the present invention is directed to the ammoxidation of isobutane to methacrylonitrile and especially of propane to acrylonitrile.

Because of the price differential between propylene and propane, an economic incentive exists for the development of a viable catalytic process for conversion of propane to acrylonitrile.

Previous attempts to develop an efficient process for the ammoxidation of propane to acrylonitrile produced either insufficient yields of acrylonitrile or processes wherein the catalyst used for the reaction did not have sufficient

lifetime characteristics to make the process economical.
For example, U.S. Patent Numbers 4,000,178, 3,833,638,
4,010,188 and 3,746,737 are related to the ammoxidation of
propane to acrylonitrile using various types of catalyst
5 systems wherein an halogen promoter is used during the
reaction. In addition, Great Britain Patent 1,333,639
relates to ammoxidation of propane using a bismuth-
molybdenum catalyst system and a halogen promoter. In each
of these cases, either the catalyst utilized does not have a
10 sufficient lifetime characteristic to make the process
economically viable or the yields of acrylonitrile obtained
during the process are unattractive from a commercial
standpoint.

More recently, U.S. Patent Numbers 4,767,739;
15 4,784,979; 4,879,264; 5,094,989; 4,837,233; and 4,877,764
are directed to propane ammoxidation to acrylonitrile
utilizing mixed metal oxide catalyst and novel procedures
for processes for preparing these catalyst which produce
improved yield. However, these systems can be improved and
20 the present invention is directed to such an improvement.

Summary of the Invention

25 It is an object of the present invention to provide an
improved process for the ammoxidation of paraffins to
unsaturated nitriles.

It is a further object of the present invention to provide a fluid bed catalytic process for the conversion of propane to acrylonitrile.

Other objects, as well as aspects, features and
5 advantages of the present invention will become apparent from the studying of the accompanying disclosure and the claims.

The foregoing and other objects of the present invention are achieved by the process of the present
10 invention, which comprises the process for the ammoxidation of a C_3 to C_5 paraffinic hydrocarbon to the corresponding unsaturated nitrile. The process comprises reacting a C_3 to C_5 paraffinic hydrocarbon with ammonia and oxygen at a temperature of between 250°C to 600°C in the presence of a
15 catalyst having the empirical formula as follows:



wherein A when present is Sn and/or Ti

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

and wherein v is 1, m is 0.5-75, a is 0 to 25, d is 0 to 25, and x is determined by the oxidation state of the cations present, and a minor quantity of an halogen-
25 containing component. Preferably, the halogen containing component is characterized by the following formula:

R-X or X_2 ,

where R=Hydrogen, C_1 - C_{20} alkyl,

and X_2 = F, Cl, Br, I or mixtures thereof.

In a preferred embodiment of the present invention the
5 paraffinic hydrocarbon is selected from the group consisting
of isobutane, propane, most preferably propane. In another
aspect of the present invention the feed may comprise a
mixture of propane and propylene.

In a still further preferred embodiment of the present
10 invention the halide component is present in the feed
mixture in an amount of between 10 to 10,000 ppm.

Preferably, the halide component is present in an amount of
between 15 to 5,000 ppm, most preferably between 20 to
1,000 ppm.

15 In another preferred embodiment of the process of the
present invention, the ratio of the oxygen-containing gas to
paraffin is between about 0.1:1 and 5:1. The ratio of
ammonia to paraffin is between 0.1:1 and 5:1. Optionally, a
diluent gas such as nitrogen may be added to the reactor.

20 The typical ratio of diluent to paraffin in the reactor can
range between 0 to 30:1. The process can be operated at an
elevated temperature of between 250°C to 800°C, preferably
between 400°C to 650°C and, most preferably, between about
460°C to 520°C.

Detailed Description of the Invention

The process of the present invention is directed to the method of preparing acrylonitrile from propane or
5 propane/propylene mixtures and methacrylonitrile from isobutane or isobutane/isobutylene mixtures. The process comprises reacting the paraffinic hydrocarbon with ammonia in an oxygen-containing-gas (preferably air) over a vanadium antimony oxide based catalyst in the presence of one or more
10 halide compounds.

The catalysts useful in the process of the present invention are described by the following empirical formula:



wherein A when present is Sn and/or Ti
15 D when present is one or more of Li, Mg, Na, Ca, Sr, Ba, Co, Fe, Cr, Ga, Ni, Zn, Ge, Nb, Zr, Mo, W, Cu, Te, Ta, Se, Bi, Ce, In, As, B, Al, P and Mn

and wherein v is 1, m is 0.5-75, a is 0 to 25, d is 0
20 to 25, and x is determined by the oxidation state of the cations present, preferably m is 0.5 to 50, a is greater than 0 to 20 and d is greater than 0 to 20, especially preferred being m equal to 0.5 to 40, a equal to 0.01 to 15 and d equal to 0.01 to 15, and a minor quantity of an
25 halogen-containing component, preferably characterized by the following formula:



where R=Hydrogen, C₁-C₂₀ alkyl

and X=F, Cl, Br, I or mixtures thereof.

These above-mentioned vanadium antimony oxide based
5 catalysts may be prepared by methods known in the art. In
particular, an effective method of preparation is the
peroxide method disclosed in U.S. Patent Numbers 4,784,979
and 4,879,264, herein incorporated by reference. In
general, the method disclosed in these patents comprises
10 making a catalyst precursor by reacting the VO(O₂)⁺ with an
antimony compound containing antimony in the valence state
of 3+. Typically the vanadium ion is made by reacting
hydrogen peroxide with a vanadium compound. This precursor
is then dried and calcined typically by spray drying to form
15 microspheroidal catalyst particles. In addition, the
catalyst may optionally be washed at any one of the points
in the procedure of making it as disclosed in U.S.
Patents 3,860,534 and 5,094,989 herein incorporated by
reference. Moreover, the catalyst may be treated by the
20 methods disclosed in U.S. Serial Numbers 112,027 and
213,325, and U.S. Serial Number 304,029, assigned to the
assignee of the present invention, herein incorporated by
reference. The catalyst may be unsupported or supported on
a suitable carrier. Preferably the catalyst is supported on
25 a carrier such as silica, alumina, zirconia and/or mixtures
thereof.

The halide compounds as described in the formula below:



where R=Hydrogen, C₁-C₂₀ alkyl

and X=F, Cl, Br, I

5 are present in the reactor in the amount of between 10 to about 10,000 ppm. Typically, the halide compound is fed to the reactor along with the paraffin, ammonia and oxygen-containing gas. Suitable halide-containing compounds useful in the practice of the present invention are hydrogen
10 bromide, hydrogen chloride, hydrogen iodide and hydrogen fluoride along with halide-alkanes such as methylbromide, methylchloride, methyliodide, methylfluoride, ethylbromide, ethylfluoride, ethyliodide, and the like. The preferred halide component is typically hydrogen bromide.

15 The contact time for the reaction would depend upon various factors, among them being the catalyst used in the surface area and the physical and chemical characteristics of the product desired. However, in general the contact times are short ranging from .1 to 20 seconds, preferably
20 between .1 to 5 seconds, most preferably being .1 to 3 seconds. The following examples of the process of the present invention are set forth below for illustration purposes only. The examples in Table 1 set forth the unexpectedly high yields of selectivities of the process of
25 the present invention combined with the unexpectedly stable performance during operation.

TABLE 1

	Catalyst Composition	Halide Promoter (ppm)	Reaction Temperature (°C)	Contact Time (sec.)	% Propane Conversion	% Acrylonitrile Selectivity	% Acrylonitrile Yield	Feed Composition
Comparative 1	EMPTY REACTOR	None 0	480	3.36	0.9	4.3	0.04	1C ₃ H ₈ /1.16NH ₃ /2.87O ₂ /10.22N ₂ /2.97H ₂ O
Comparative 2	EMPTY REACTOR	HBr 378	480	3.36	2.2	1.1	0.02	1C ₃ H ₈ /1.16NH ₃ /2.87O ₂ /10.22N ₂ /2.97H ₂ O
Comparative 3	Quartz Chips	HBr 378	480	3.17	1.7	0.0	0.00	1C ₃ H ₈ /1.16NH ₃ /2.87O ₂ /10.22N ₂ /2.97H ₂ O
Comparative 4	VSb _{1.4} Sn _{0.2} Ti _{0.1} O _x	None 0	480	3.02	41.7	42.7	17.78	1C ₃ H ₈ /1.16NH ₃ /2.87O ₂ /10.22N ₂ /2.97H ₂ O
Example 1	VSb _{1.4} Sn _{0.2} Ti _{0.1} O _x	C ₂ H ₅ Br 1363	470	2.06	90.7	46.8	42.48	1C ₃ H ₈ /1.25NH ₃ /2.98O ₂ /10.68N ₂ /2.91H ₂ O
Example 2	VSb _{1.4} Sn _{0.2} Ti _{0.1} O _x	HBr 1363	470	2.10	87.3	50.8	44.30	1C ₃ H ₈ /1.25NH ₃ /2.98O ₂ /10.68N ₂ /2.91H ₂ O
Example 3	VSb _{1.4} Sn _{0.2} Ti _{0.1} O _x	HBr 351	470	4.28	89.0	48.1	42.81	1C ₃ H ₈ /1.16NH ₃ /2.99O ₂ /10.75N ₂ /2.88H ₂ O
Example 4	VSb _{1.4} Sn _{0.2} Ti _{0.1} O _x	HBr 1359	470	2.95	94.2	45.9	43.21	1C ₃ H ₈ /1.25NH ₃ /2.99O ₂ /10.69N ₂ /2.91H ₂ O
Example 5	VSb _{1.4} Sn _{0.2} Ti _{0.1} O _x	HBr 1847	450	2.94	90.4	50.1	45.29	1C ₃ H ₈ /1.24NH ₃ /2.97O ₂ /10.65N ₂ /3.05H ₂ O
Example 6	VSb _{1.4} Sn _{0.2} Ti _{0.1} O _x	HBr 2607	460	1.76	87.5	48.1	42.12	1C ₃ H ₈ /1.34NH ₃ /2.97O ₂ /10.65N ₂ /2.93H ₂ O
Comparative 5	VSb _{1.4} Sn _{0.2} Ti _{0.1} O _x	None 0	480	3.59	29.9	55.7	16.68	3C ₃ H ₈ /1.20NH ₃ /2.88O ₂ /10.04N ₂ /1.86H ₂ O
Example 7	VSb _{1.4} Sn _{0.2} Ti _{0.1} O _x	HBr 78	480	2.10	31.8	59.6	18.92	3C ₃ H ₈ /1.41NH ₃ /2.82O ₂ /9.70N ₂ /1.91H ₂ O
Example 8	VSb _{1.4} Sn _{0.2} Ti _{0.1} O _x	HBr 138	460	3.39	30.1	61.6	18.54	3C ₃ H ₈ /1.22NH ₃ /3.03O ₂ /10.82N ₂ /3.69H ₂ O
Comparative 6	VSb _{1.4} Sn _{0.2} Ti _{0.1} O _x	None 0	460	4.06	24.4	56.8	13.85	3C ₃ H ₈ /1.21NH ₃ /3.03O ₂ /2.91N ₂ /1.37H ₂ O
Example 9	VSb _{1.4} Sn _{0.2} Ti _{0.1} O _x	HBr 173	460	4.13	31.3	60.0	18.80	3C ₃ H ₈ /1.24NH ₃ /3.03O ₂ /2.91N ₂ /1.40H ₂ O

TABLE 1

	Catalyst Composition	Halide Promoter (ppm)	Reaction Temperature (°C)	Contact Time (sec.)	% Propane Conversion	% Acrylonitrile Selectivity	% Acrylonitrile Yield	Feed Composition
Example 10	$\text{VSb}_{1.2}\text{Sn}_{0.5}\text{Ti}_{1.0}\text{Fe}_{0.12}\text{O}_x + 40\% \text{SiO}_2$	$\text{C}_2\text{H}_5\text{Br}$ 1982	460	1.36	89.8	43.3	38.86	$1\text{C}_3\text{H}_8/1.23\text{NH}_3/3.20\text{O}_2/11.41\text{N}_2/3.30\text{H}_2\text{O}$
Example 11	$\text{VSb}_{1.2}\text{Sn}_{0.5}\text{Ti}_{1.0}\text{Fe}_{0.12}\text{O}_x + 40\% \text{SiO}_2$	HBr 951	480	1.87	87.9	37.3	32.78	$1\text{C}_3\text{H}_8/1.30\text{NH}_3/3.00\text{O}_2/10.65\text{N}_2/5.05\text{H}_2\text{O}$
Example 12	$\text{VSb}_{1.2}\text{Sn}_{0.5}\text{Ti}_{1.0}\text{Fe}_{0.12}\text{O}_x + 40\% \text{SiO}_2$	HBr 534	480	1.25	85.2	55.1	46.88	$0.419\text{C}_3\text{H}_8/0.581\text{C}_3\text{H}_8/1.3\text{NH}_3/2.94\text{O}_2/10.45\text{N}_2/3.02\text{H}_2\text{O}$
Example 13	$\text{VSb}_{1.2}\text{Sn}_{0.5}\text{Ti}_{1.0}\text{Fe}_{0.12}\text{O}_x + 40\% \text{SiO}_2$	HBr 511	480	1.60	87.2	52.2	45.50	$0.417\text{C}_3\text{H}_8/0.583\text{C}_3\text{H}_8/1.3\text{NH}_3/2.90\text{O}_2/10.31\text{N}_2/4.04\text{H}_2\text{O}$
Example 14	$[\text{VSb}_{1.4}\text{Sn}_{0.2}\text{Ti}_{0.1}\text{O}_x + \text{Sb}_{0.2}]\text{Co}_{0.001}$	HBr 1343	470	2.56	92.5	48.2	44.60	$1\text{C}_3\text{H}_8/1.28\text{NH}_3/2.92\text{O}_2/10.44\text{N}_2/2.80\text{H}_2\text{O}$
Example 15	$[\text{VSb}_{1.4}\text{Sn}_{0.2}\text{Ti}_{0.1}\text{O}_x + \text{Sb}_{0.2}]\text{Co}_{0.05}$	HBr 38	480	2.06	29.2	63.6	18.59	$3\text{C}_3\text{H}_8/1.66\text{NH}_3/2.83\text{O}_2/9.97\text{N}_2/1.90\text{H}_2\text{O}$
Example 16	$[\text{VSb}_{1.4}\text{Sn}_{0.2}\text{Ti}_{0.1}\text{O}_x + \text{Sb}_{0.2}]\text{Co}_{0.05}$	HBr 73	480	2.14	30.0	63.0	18.91	$3\text{C}_3\text{H}_8/1.66\text{NH}_3/2.83\text{O}_2/9.97\text{N}_2/1.89\text{H}_2\text{O}$
Example 17	$\text{VSb}_{1.8}\text{Sn}_{0.2}\text{Ti}_{0.01}\text{O}_x$	HBr 1037	480	2.15	92.1	43.8	40.37	$1\text{C}_3\text{H}_8/1.28\text{NH}_3/2.92\text{O}_2/10.44\text{N}_2/3.48\text{H}_2\text{O}$
Example 18	$\text{VSb}_{2.0}\text{Sn}_{0.25}\text{O}_x$	HBr 1903	470	1.76	91.5	42.7	39.04	$1\text{C}_3\text{H}_8/1.28\text{NH}_3/3.00\text{O}_2/10.67\text{N}_2/3.13\text{H}_2\text{O}$
Example 19	$\text{VSb}_{3.9}\text{Sn}_{1.2}\text{Cu}_{3.8}\text{Te}_{1.7}\text{W}_{0.7}\text{O}_x$	HBr 1902	460	3.78	95.0	46.0	43.67	$1\text{C}_3\text{H}_8/1.15\text{NH}_3/3.33\text{O}_2/10.70\text{N}_2/3.22\text{H}_2\text{O}$
Comparative 7	$\text{VSb}_{1.4}\text{Sn}_{0.2}\text{Ti}_{0.1}\text{O}_x$	None 0	480	3.59	40.3	47.5	19.12	$1\text{C}_3\text{H}_8/1.18\text{NH}_3/2.92\text{O}_2/10.46\text{N}_2/0.00\text{H}_2\text{O}$
Example 20	$\text{VSb}_{1.4}\text{Sn}_{0.2}\text{Ti}_{0.1}\text{O}_x$	CCl_4 474	480	3.52	54.0	47.4	25.60	$1\text{C}_3\text{H}_8/1.18\text{NH}_3/2.92\text{O}_2/10.46\text{N}_2/0.00\text{H}_2\text{O}$
Example 21	$\text{VSb}_{1.4}\text{Sn}_{0.2}\text{Ti}_{0.1}\text{O}_x$	CCl_4 946	480	3.57	60.9	46.8	28.48	$1\text{C}_3\text{H}_8/1.18\text{NH}_3/2.92\text{O}_2/10.46\text{N}_2/0.00\text{H}_2\text{O}$
Example 22	$\text{VSb}_{1.4}\text{Sn}_{0.2}\text{Ti}_{0.1}\text{O}_x$	CHCl_3 1314	480	3.51	57.8	45.3	26.15	$1\text{C}_3\text{H}_8/1.16\text{NH}_3/2.89\text{O}_2/10.32\text{N}_2/0.00\text{H}_2\text{O}$



What we claim as our invention is:

1. The process for the ammoxidation of a C₃ to C₅ paraffinic hydrocarbon to its corresponding α,β -unsaturated hydrocarbon comprising reacting the C₃ to C₅ paraffinic hydrocarbon with ammonia and oxygen in a fluid bed reactor at a temperature of between 250°C to 600°C in the presence of a catalyst having the empirical formula as follows:



wherein A when present is Sn and/or Ti

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

wherein v is 1, m is 0.5-75, a is 0 to 25, d is 0 to 15 25, and x is determined by the oxidation state of the cations present, and a minor quantity of an halogen-containing component.

2. The process of claim 1 wherein the halogen-containing component is characterized by the following 20 formula:



where R=Hydrogen, C₁-C₂₀ alkyl

and X=F, Cl, Br, I or mixtures thereof.

3. The process of claim 1 wherein the halogen 25 containing component is characterized by the following formula:





where X=F, Cl, Br, I or mixtures thereof.

4. The process of claim 1 wherein the paraffinic hydrocarbon is selected from the group consisting of isobutane and propane.

5 5. The process of claim 4 wherein the paraffinic hydrocarbon is propane.

6. The process of claim 1 wherein the halogen containing compound is present in the feed mixture in an amount of between 10 to 10,000 ppm.

10 7. The process of claim 6 wherein the halogen containing compound is present in an amount of between 15 to 5,000 ppm.

8. The process of claim 7 wherein the halogen containing compound is present in an amount between 20 to 15 1,000 ppm.

9. The process of claim 2 wherein the halogen containing compound is selected from the group consisting of hydrogen bromide, hydrogen chloride, methyl bromine, methyl chloride, hydrogen iodide, hydrogen fluorine, methyl iodide 20 and methyl fluorine.

10. The process of claim 9 wherein the halogen containing compound is selected to be hydrogen bromide.

11. The process of claim 1 wherein the halogen containing compound is added to the reactor along with the 25 paraffinic hydrocarbon, ammonia and oxygen.

12. The process of claim 1 wherein the halogen containing compound is added to the catalyst.