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Paraffin ammoxidation using vanadium antimony oxide based catalysts with halide promoters
Ammoxidation von Paraffinen unter Verwendung von auf Vanadium-Antimonoxid basierenden Katalysatoren mit Halidpromotoren
Ammoxydation de paraffines par l'utilisation de catalyseurs à base de vandium antimoine oxydes contenant un promoteur à base d'halogénure

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References cited:
EP-A-0 337 028
US-A-4 010 188

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Description

[0001] The invention relates to an improved process for the catalytic ammoxidation of paraffins containing from 3 to 5 carbon atoms to \( \alpha, \beta \)-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.

[0002] 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.

[0003] 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 4,000,175, 3,833,639, 4,010,188 and 3,746,737 are related to the ammoxidation of propane to acrylonitrile using various types of catalyst 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 sufficient lifetime characteristic to make the process economically viable or the yields of acrylonitrile obtained during the process are unattractive from a commercial standpoint.

[0004] More recently, U.S. Patent Numbers 4,757,739; 4,784,979; 4,879,264; 5,094,988; 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 the present invention is directed to such an improvement.

Summary of the Invention

[0005] It is an object of the present invention to provide an improved process for the ammoxidation of paraffins to unsaturated nitriles.

[0006] It is a further object of the present invention to provide a fluid bed catalytic process for the conversion of propane to acrylonitrile.

[0007] Other objects, as well as aspects, features and advantages of the present invention will become apparent from the studying of the accompanying disclosure and the claims.

[0008] The foregoing and other objects of the present invention are achieved by the process of the present invention, which comprises the process for the ammoxidation of a \( C_3 \) to \( C_6 \) paraffinic hydrocarbon to the corresponding unsaturated nitrile. The process comprises reacting a \( C_3 \) to \( C_6 \) paraffinic hydrocarbon with ammonia and oxygen at a temperature of between 250°C to 600°C in the presence of a catalyst having the empirical formula as follows:

\[
V_xSb_mA_nD_oO_x
\]

wherein

\( A \) when present in 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, 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 an halogen-containing component in an amount between 10 to 10000 ppm. Preferably, the halogen containing component is characterized by the following formula:

\[ R-X \text{ or } X_2. \]

where \( R \) is Hydrogen, \( C_1-C_{20} \) alkyl, and \( X = F, Cl, Br, I \) or mixtures thereof.

[0009] In a preferred embodiment of the present invention the 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.

[0010] 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.
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. 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 450°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 propylene mixtures and methacrylonitrile from isobutane or isobutene/isobutylene mixtures. The process comprises reacting the paraffinic hydrocarbon with ammonia in an oxygen-containing gas (preferably air) over a vanadium antimony oxide catalyst in the presence of one or more halide compounds.

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

\[ V_x Sb_y A_z D_d O_x \]

wherein A when present in 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, W, Cu, Te, Ta, Se, Bi, Ce, In, As, B, Al, P and Mn

and wherein \( v \) is 1, \( m \) is 0.75, \( a \) is 0 to 25, \( d \) is 0 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 an halogen-containing component in an amount of between 10 to 10,000 ppm, preferably characterized by the following formula:

\[ R \cdot X \text{ or } X_2 \]

where \( R \) is Hydrogen, \( C_1 \text{ to } C_{20} \) alkyl, and \( X = F, Cl, Br, I \) or mixtures thereof.

These above-mentioned vanadium antimony oxide based 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 4,794,979 and 4,879,264. In general, the method disclosed in these patents comprises making a catalyst precursor by reacting the \( VO(O_2)^+ \) 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 microspherical 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 3,660,534 and 5,094,989. Moreover, the catalyst may be treated by the methods disclosed in US 5,432,141 (USSN 213,325), US 5,496,588 (USSN 304,029) and US 5,696,067 (USSN 453,567 a continuation application based on USSN 112,027), assigned to the assignee of the present invention. The catalyst may be unsupported or supported on a suitable carrier. Preferably the catalyst is supported on a carrier such as silica, alumina, zirconia and/or mixtures thereof.

The halide compounds as described in the formula below:

\[ R \cdot X \text{ or } X_2 \]

where \( R \) is Hydrogen, \( C_1 \text{ to } C_{20} \) alkyl and \( X = F, Cl, Br, I \) are present in the reactor in the amount of between 10 to 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 bromide, hydrogen chloride, hydrogen iodide and hydrogen fluoride along with halide-alkanes such as methyl bromide, methyl chloride, methyl iodide, methyl fluoride, ethyl bromide, ethyl fluoride, ethyl iodide, and the like. The preferred halide component is typically hydrogen bromide.

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 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 the present invention combined with the unexpectedly stable performance during operation.
<table>
<thead>
<tr>
<th></th>
<th>Catalyst Composition</th>
<th>Haide Promoter (ppm)</th>
<th>Reaction Temperature (°C)</th>
<th>Contact Time (sec.)</th>
<th>% Propane Conversion</th>
<th>% Acrylonitrile Selectivity</th>
<th>% Acrylonitrile Yield</th>
<th>Feed Composition</th>
</tr>
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<tbody>
<tr>
<td>Comparative 1</td>
<td>EMPTY REACTOR</td>
<td>None 0</td>
<td>480</td>
<td>3.36</td>
<td>0.9</td>
<td>4.3</td>
<td>0.04</td>
<td>1C₂H₅/1.16NH₃/2.87O₂/10.22N₂/2.97H₂O</td>
</tr>
<tr>
<td>Comparative 2</td>
<td>EMPTY REACTOR</td>
<td>HBr 378</td>
<td>480</td>
<td>3.36</td>
<td>2.2</td>
<td>1.1</td>
<td>0.02</td>
<td>1C₂H₅/1.16NH₃/2.87O₂/10.22N₂/2.97H₂O</td>
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<tr>
<td>Comparative 3</td>
<td>Quartz Chips</td>
<td>HBr 378</td>
<td>480</td>
<td>3.17</td>
<td>1.7</td>
<td>0.0</td>
<td>0.00</td>
<td>1C₂H₅/1.16NH₃/2.87O₂/10.22N₂/2.97H₂O</td>
</tr>
<tr>
<td>Comparative 4</td>
<td>VSB₁₆Sn₁₁Te₁₁O₁₁</td>
<td>None 0</td>
<td>480</td>
<td>3.02</td>
<td>41.7</td>
<td>42.7</td>
<td>17.78</td>
<td>1C₂H₅/1.16NH₃/2.87O₂/10.22N₂/2.97H₂O</td>
</tr>
<tr>
<td>Example 1</td>
<td>VSB₁₆Sn₁₁Te₁₁O₁₁</td>
<td>C₅H₇Br 1363</td>
<td>470</td>
<td>2.06</td>
<td>90.7</td>
<td>46.6</td>
<td>42.48</td>
<td>1C₂H₅/1.25NH₃/2.99O₂/10.68N₂/2.91H₂O</td>
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<td>Example 2</td>
<td>VSB₁₆Sn₁₁Te₁₁O₁₁</td>
<td>HBr 1363</td>
<td>470</td>
<td>2.10</td>
<td>87.3</td>
<td>50.8</td>
<td>44.30</td>
<td>1C₂H₅/1.25NH₃/2.99O₂/10.68N₂/2.91H₂O</td>
</tr>
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<td>Example 3</td>
<td>VSB₁₆Sn₁₁Te₁₁O₁₁</td>
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<td>470</td>
<td>4.28</td>
<td>89.0</td>
<td>48.1</td>
<td>42.81</td>
<td>1C₂H₅/1.16NH₃/2.99O₂/10.75N₂/2.88H₂O</td>
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<td>Example 4</td>
<td>VSB₁₆Sn₁₁Te₁₁O₁₁</td>
<td>HBr 1359</td>
<td>470</td>
<td>2.95</td>
<td>94.2</td>
<td>45.9</td>
<td>43.21</td>
<td>1C₂H₅/1.25NH₃/2.99O₂/10.69N₂/2.91H₂O</td>
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<td>Example 5</td>
<td>VSB₁₆Sn₁₁Te₁₁O₁₁</td>
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<td>2.94</td>
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<td>45.29</td>
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<td>Example 6</td>
<td>VSB₁₆Sn₁₁Te₁₁O₁₁</td>
<td>HBr 2007</td>
<td>460</td>
<td>1.76</td>
<td>87.5</td>
<td>48.1</td>
<td>42.12</td>
<td>1C₂H₅/1.34NH₃/2.97O₂/10.65N₂/2.93H₂O</td>
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<td>Comparative 5</td>
<td>VSB₁₆Sn₁₁Te₁₁O₁₁</td>
<td>None 0</td>
<td>480</td>
<td>3.59</td>
<td>29.9</td>
<td>55.7</td>
<td>16.65</td>
<td>3C₂H₅/1.20NH₃/2.88O₂/10.04N₂/1.93H₂O</td>
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<tr>
<td>Example 7</td>
<td>VSB₁₆Sn₁₁Te₁₁O₁₁</td>
<td>HBr 178</td>
<td>480</td>
<td>2.10</td>
<td>31.8</td>
<td>59.6</td>
<td>18.92</td>
<td>3C₂H₅/1.41NH₃/2.82O₂/9.70N₂/1.91H₂O</td>
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<td>Example 8</td>
<td>VSB₁₆Sn₁₁Te₁₁O₁₁</td>
<td>HBr 138</td>
<td>460</td>
<td>3.39</td>
<td>30.1</td>
<td>61.6</td>
<td>18.54</td>
<td>3C₂H₅/1.22NH₃/3.03O₂/10.82N₂/3.63H₂O</td>
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<tr>
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<td>VSB₁₆Sn₁₁Te₁₁O₁₁</td>
<td>None 0</td>
<td>460</td>
<td>4.05</td>
<td>24.4</td>
<td>56.6</td>
<td>13.85</td>
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<tr>
<td>Example 9</td>
<td>VSB₁₆Sn₁₁Te₁₁O₁₁</td>
<td>HBr 173</td>
<td>460</td>
<td>4.13</td>
<td>31.3</td>
<td>60.0</td>
<td>18.80</td>
<td>3C₂H₅/1.24NH₃/3.03O₂/2.91N₂/1.40H₂O</td>
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<tr>
<td>Example</td>
<td>Catalyst Composition</td>
<td>Halide Promoter (ppm)</td>
<td>Reaction Temperature (°C)</td>
<td>Contact Time (sec.)</td>
<td>% Propane Conversion</td>
<td>% Acrylonitrile Selectivity</td>
<td>% Acrylonitrile Yield</td>
<td>Feed Composition</td>
</tr>
<tr>
<td>---------</td>
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<td>---------------------</td>
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<tr>
<td>10</td>
<td>VSB₁₃Sn₂₃Ti₁₆Fe₃₂O₄₆</td>
<td>C₂H₅Br 1982</td>
<td>460</td>
<td>1.36</td>
<td>89.6</td>
<td>43.3</td>
<td>38.86</td>
<td>1C₃H₈/1.23NH₃/3.20O₂/11.41N₂/3.30H₂O</td>
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<td>HBr 971</td>
<td>460</td>
<td>1.87</td>
<td>87.9</td>
<td>37.3</td>
<td>32.76</td>
<td>1C₃H₈/1.30NH₃/3.00O₂/10.65N₂/5.05H₂O</td>
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<td>VSB₁₃Sn₂₃Ti₁₆Fe₃₂O₄₆</td>
<td>HBr 534</td>
<td>460</td>
<td>1.25</td>
<td>85.2</td>
<td>55.1</td>
<td>46.88</td>
<td>0.419C₂H₅/0.581C₂H₅/1.3NH₂/2.94O₂/10.45N₂/3.02H₂O</td>
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<td>VSB₁₃Sn₂₃Ti₁₆Fe₃₂O₄₆</td>
<td>HBr 511</td>
<td>460</td>
<td>1.60</td>
<td>87.2</td>
<td>52.2</td>
<td>45.50</td>
<td>0.417C₂H₅/0.583C₂H₅/1.3NH₂/2.90O₂/10.31N₂/4.04H₂O</td>
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<td>[VSB₁₃Sn₂₃Te₁₆O₄₆]*</td>
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<td>470</td>
<td>2.55</td>
<td>92.5</td>
<td>48.2</td>
<td>44.00</td>
<td>1C₂H₅/1.28NH₂/2.92O₂/10.44N₂/2.80H₂O</td>
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<td>15</td>
<td>[VSB₁₃Sn₂₃Te₁₆O₄₆]*</td>
<td>HBr 38</td>
<td>460</td>
<td>2.06</td>
<td>29.2</td>
<td>63.6</td>
<td>18.59</td>
<td>3C₂H₅/1.66NH₂/2.83O₂/9.97N₂/1.90H₂O</td>
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<td>16</td>
<td>[VSB₁₃Sn₂₃Te₁₆O₄₆]*</td>
<td>HBr 73</td>
<td>480</td>
<td>2.14</td>
<td>30.0</td>
<td>63.0</td>
<td>18.91</td>
<td>3C₂H₅/1.66NH₂/2.83O₂/9.97N₂/1.69H₂O</td>
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<td>VSB₁₃Sn₂₃Te₁₆O₄₆</td>
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<td>480</td>
<td>2.15</td>
<td>92.1</td>
<td>43.8</td>
<td>40.37</td>
<td>1C₂H₅/1.28NH₂/2.92O₂/10.44N₂/3.48H₂O</td>
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<td>18</td>
<td>VSB₁₃Sn₂₃Te₁₆O₄₆</td>
<td>HBr 1903</td>
<td>470</td>
<td>1.70</td>
<td>91.5</td>
<td>42.7</td>
<td>39.04</td>
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<td>19</td>
<td>VSB₁₃Sn₂₃Te₁₆O₄₆</td>
<td>HBr 1902</td>
<td>460</td>
<td>3.78</td>
<td>95.0</td>
<td>46.0</td>
<td>43.67</td>
<td>1C₂H₅/1.15NH₃/3.33O₂/10.70N₂/0.22H₂O</td>
</tr>
<tr>
<td>Comparative 7</td>
<td>VSB₁₃Sn₂₃Te₁₆O₄₆</td>
<td>None</td>
<td>480</td>
<td>3.59</td>
<td>40.3</td>
<td>47.5</td>
<td>19.12</td>
<td>1C₂H₅/1.18NH₂/2.92O₂/10.46N₂/0.00H₂O</td>
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<td>20</td>
<td>VSB₁₃Sn₂₃Te₁₆O₄₆</td>
<td>CHCl₃ 474</td>
<td>480</td>
<td>3.52</td>
<td>54.0</td>
<td>47.4</td>
<td>25.60</td>
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<td>480</td>
<td>3.57</td>
<td>60.9</td>
<td>46.8</td>
<td>28.48</td>
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<td>3.51</td>
<td>57.8</td>
<td>45.3</td>
<td>26.15</td>
<td>1C₂H₅/1.16NH₂/2.85O₂/10.32N₂/0.00H₂O</td>
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EP 0 747 349 B1

Claims

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:

\[ V_{n}Sb_{m}A_{a}D_{d}O_{x} \]

wherein

A when present in 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, 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 an halogen-containing component in an amount between 10 to 1,000 ppm.

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

\[ R-X \]

where R=Hydrogen, C1-C20 alkyl,

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

3. 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 and methyl fluorine.

4. The process of claim 3 wherein the halogen containing compound is selected to be hydrogen bromide.

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

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

6. The process of any preceding claim wherein the paraffinic hydrocarbon is selected from the group consisting of isobutane and propane.

7. The process of claim 6 wherein the paraffinic hydrocarbon is propane.

8. The process of any preceding claim wherein the halogen containing compound is present in the feed mixture in an amount of between 15 to 5,000 ppm.

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

10. The process of any preceding claim wherein the halogen containing compound is added to the reactor along with the paraffinic hydrocarbon, ammonia and oxygen.

11. The process of any one of claims 1 to 9 wherein the halogen containing compound is added to the catalyst.

Reivendications

1. Le procédé pour l'ammoxydation d'un hydrocarbure paraffinique C₃ à C₅ jusqu'à son hydrocarbure α,β-insaturé correspondant comportant la réaction de l'hydrocarbure paraffinique C₃ à C₅ avec l'ammoniac et l'oxygène dans un réacteur à lit fluide à une température comprise entre 250°C et 600°C en présence d'un catalyseur ayant la formule empirique suivante:
dans laquelle

A. lorsque présent, est Sn et/ou Ti

D. lorsque présent, est un ou davantage de 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 et Mn

e et dans laquelle v est l, m est 0.5 à 75, a est 0 à 25, d est 0 à 25 et x est déterminé par l'état d'oxydation des cations présents, et un composant contenant des halogènes en une quantité comprise entre 10 et 1.000 ppm.

2. Le procédé de la revendication 1, dans lequel le composant contenant des halogènes est caractérisé par la formule suivante :

R-X

dans laquelle

R = hydrogène, C₁-C₂₀ alkyle,
et X=F, Cl, Br, l ou des mélanges de ceux-ci.

3. Le procédé de la revendication 2, dans lequel le composant est sélectionné parmi le groupe comportant le bromure d'hydrogène, le chlorure d'hydrogène, le bromure de méthyle, le chlorure de méthyle, l'iodyure d'hydrogène, le fluorure d'hydrogène, l'iodyure de méthyle et le fluorure de méthyle.

4. Le procédé de la revendication 3, dans lequel le composant est sélectionné pour être le bromure d'hydrogène.

5. Le procédé de la revendication 1, dans lequel le composant est caractérisé par la formule suivante :

X₂

dans laquelle X=F, Cl, Br, l ou des mélanges de ceux-ci.

6. Le procédé selon l'une quelconque des revendications précédentes, dans lequel l'hydrocarbure paraffinique est sélectionné parmi le groupe comportant l'isobutane et le propane.

7. Le procédé de la revendication 6, dans lequel l'hydrocarbure paraffinique est le propane.

8. Le procédé selon l'une quelconque des revendications précédentes, dans lequel le composé contenant des halogènes est présent dans le mélange de charge en une quantité comprise entre 15 et 5.000 ppm.

9. Le procédé de la revendication 8, dans lequel le composé contenant des halogènes est présent en une quantité comprise entre 20 et 1.000 ppm.

10. Le procédé selon l'une quelconque des revendications précédentes, dans lequel le composé contenant des halogènes est ajouté au réacteur avec l'hydrocarbure paraffinique, l'ammoniac et l'oxygène.

11. Le procédé selon l'une quelconque des revendications 1 à 9, dans lequel le composé contenant des halogènes est ajouté au catalyseur.

Patentansprüche

1. Das Verfahren für die Ammonoxidation eines C₅⁻ bis C₆⁻paraffinischen Kohlenwasserstoffs zu seinem entsprechenden α,β-unsgesättigten Kohlenwasserstoff, umfassend die Reaktion des C₅⁻ bis C₆⁻paraffinischen Kohlenwasser-
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stoffe mit Ammoniak und Sauerstoff in einem Fließbett-Reaktor bei einer Temperatur von zwischen 250°C bis 600°C in Anwesenheit eines Katalysators mit der empirischen Formel wie folgt:

\[ V_{(v)} Sb_m A_a D_d O_x \]

worin

A, wenn vorhanden, Sn und/oder Ti ist,
D, wenn vorhanden, eines oder mehrere der Elemente 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 und Mn ist

und worin v 1 ist, m 0.5-75 ist, a 0 bis 25 ist, d 0 bis 25 ist, und x durch den Oxidationszustand der vorhandenen Kationen bestimmt ist, und einer Halogen-enenthaltenden Komponente in einer Menge zwischen 10 bis 1000 ppm.

2. Das Verfahren von Anspruch 1, worin die Halogen-enenthaltende Komponente durch die nachfolgende Formel gekennzeichnet ist:

\[ R-X \]

worin R = Wasserstoff, C_1- bis C_20-Alkyl,
und X = F, Cl, Br, I, oder Mischungen derselben.


4. Das Verfahren von Anspruch 3, worin die Halogen-enenthaltende Verbindung ausgewählt ist, um Bromwasserstoff zu sein.

5. Das Verfahren von Anspruch 1, worin die Halogen-enenthaltende Komponente gekennzeichnet ist durch die folgende Formel:

\[ X_2 \]

worin X = F, Cl, Br, I, oder Mischungen derselben.

6. Das Verfahren nach irgendeinem der vorstehenden Ansprüche, worin der paraffinische Kohlenwasserstoff aus der Gruppe bestehend aus Isobutan und Propan ausgewählt ist.

7. Das Verfahren von Anspruch 6, worin der paraffinische Kohlenwasserstoff Propan ist.

8. Das Verfahren nach irgendeinem der vorstehenden Ansprüche, worin die Halogen-enenthaltende Verbindung in der Beschickungsmischung in einer Menge von zwischen 15 bis 5000 ppm vorhanden ist.

9. Das Verfahren von Anspruch 6, worin die Halogen-enenthaltende Verbindung in einer Menge von zwischen 20 bis 1000 ppm vorhanden ist.


11. Das Verfahren von irgendeinem der Ansprüche 1 bis 9, worin die Halogen-enenthaltende Verbindung zu dem Katalysator zugesetzt ist.