

PATENT SPECIFICATION

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(54) PROCESS FOR THE PREPARATION OF ETHYLENE NITRILES

(71) We, PRODUITS CHIMIQUES UGINE KUHLMANN, a French Body Corporate, of 25, Boulevard de l'Amiral Bruix, Paris 16°, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to a process for the preparation of ethylene nitriles from olefins, and in particular acrylonitrile from propene and methacrylonitrile from isobutene.

15 Numerous catalysts have previously been proposed, for example in French Patent Specifications Nos. 1,247,785, 1,261,568 and 1,293,088 for the catalytic ammoxidation of olefins into ethylene nitriles, but the yields and selectivities which they make it possible to obtain are far from being quantitative, and further progress is desirable for the sake of the economy of the production of these important industrial products, particularly acrylonitrile.

25 We have found that by using the catalyst described below very high selectivities for unsaturated nitriles can be obtained with high olefin conversion rates; this leads to excellent yields in relation to the olefin used.

30 According to the invention ethylene nitriles are prepared by the catalytic oxidation in the vapour phase, of an olefin in the presence of ammonia, the catalyst containing, in addition to oxygen, the following elements: cobalt, iron, bismuth, tungsten, molybdenum and optionally silicon, and also an element Z selected from group Ia or group IIa of the Periodic Table according to Mendeleef, the proportions of the elements being so selected that their atomic ratios are within the following ranges:

35 Co/Fe/Bi/W/Mo/Si/Z = 2.0-20.0 / 0.1-10.0 / 0.1-10.0 / 0.5-10.0 / 2-11.5 / 0-15.0 / 45 0.005-1.0 and the sum of the atomic ratios

of molybdenum and tungsten is 12.

Suitably the element from group Ia is lithium, sodium potassium, rubidium or cesium. The element from group IIa is possibly beryllium, magnesium, calcium, strontium or barium.

The oxygen content of the catalyst can be varied. It is determined in accordance with the proportion of metallic elements which are present in the catalyst in the form of complex oxides or of oxyacids.

The catalyst used in the invention can be prepared, for example, by mixing aqueous solutions of ammonium molybdate and ammonium paratungstate, to which there are then added solutions of cobalt, iron, and bismuth nitrates, followed by a hydroxide or a carbonate of an alkali metal or of a metal of the previously mentioned group IIa, in the form of a powder, suspension, or aqueous solution, depending on its solubility, followed by the addition of colloidal silica as a source of silicon. The medium is then evaporated and the catalyst is formed into grains, rods, or pastilles by any known means, for example by extrusion of a paste or formation of a powder into pastilles, and is then calcined at a temperature between 350°C and 600°C in a current of air. The raw materials indicated by way of example are not limitative, and salts other than the ammonium salts, nitrates, hydroxides, or carbonates indicated may be used provided that their calcination produces metal oxides.

Various supports or diluents may also be used, such as silica gel, alumina, silicon carbide, diatomaceous earths, titanium oxide (rutile or anatase) and "Celite" for example, the preferred supports being silica gel, titanium oxide, and "Celite" (CELITE is a Registered Trade Mark).

The catalytic ammoxidation of the olefin is usually effected in the gas phase by passing over a layer of the catalyst a gaseous mixture composed of 1 to 10 volume %

olefin, 1 to 10 volume % ammonia, 5-15 volume % molecular oxygen, 20-60 volume % water vapour, and 20-60 volume % of an inert gas, for example nitrogen, at a temperature between 250 and 500°C and under a total pressure close to atmospheric pressure, preferably between 1 and 2 bars. Suitable contact times are of the order of 1 to 10 seconds. The catalyst may be dis-

posed in a fixed bed, for example in a 10 multibar reactor, or in a fluidised bed.

By operating under the conditions thus described it is possible to obtain, for example with propene, practically quantitative conversion rates with a selectivity of 15 acrylonitrile higher than 80%.

The expressions conversion, selectivity, and yield are defined as follows:

$$\begin{aligned} \text{Conversion \%} &= \frac{\text{Number of moles of reacted olefin}}{\text{Number of moles of olefin introduced}} \times 100 \\ \text{Selectivity \%} &= \frac{\text{Number of moles of ethylene nitrile formed}}{\text{Number of moles of reacted olefin}} \times 100 \\ \text{Yield \%} &= \frac{\text{Number of moles of ethylene nitrile formed}}{\text{Number of moles of olefin introduced}} \times 100 \end{aligned}$$

The invention will now be described with reference to the following Examples:

EXAMPLE 1

70.0 g cobalt nitrate are dissolved in 20 cc distilled water. 24.3 g ferric nitrate are also dissolved in 20 cc distilled water, and 29.2 g bismuth nitrate in 30 cc distilled water are acidified by 6 cc concentrated nitric acid. In addition, 106.2 g ammonium molybdate and 32.4 g ammonium paratungstate are dissolved in 150 g water. The three aqueous solutions of nitrates are then introduced drop by drop into the aqueous solution of ammonium salts, whereupon a solution of 0.202 g potassium hydroxide in 15 g water and 24.4 g of a silica sol containing 20% by weight of SiO_2 are added. The resulting suspension is heated under agitation, and the liquid is evaporated. The resulting solid product is then calcined at 450°C for 6 hours in a current of air. The catalyst obtained in this manner has the following composition, expressed in atomic ratios of the elements:



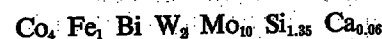
60 cc of catalyst in the forms of grains of 3-5 mm are placed in a glass reactor composed of a U-tube with an inside diameter of 12 mm and immersed in a bath of molten alkali metal nitrates heated electrically at 420°C. Into this reactor are passed 54 litres per hour of a gaseous mixture having the following composition by volume:

propene	5.7 %
propane	0.3 %
ammonia	7.0 %
air	65.0 %
water vapour	22.0 %

Under these conditions measurement shows that the propene conversion rate attains 94.3 % and that the selectivity in respect of acrylonitrile attains 83.5 %; the yield of acrylonitrile is therefore 78.8%. 6.6% of the propene introduced was, moreover, converted into carbon oxides.

EXAMPLE 2

The operation is carried out in the same manner as in Example 1, both for the preparation of the catalyst and for the ammoxidation test, but in the preparation of the catalyst the 0.202 g potassium hydroxide was replaced by 0.266 g calcium hydroxide. The catalyst obtained in this manner has the following composition, expressed in atomic ratios of the elements:



The propene conversion rate attains 92.7 % with a selectivity in respect of acrylonitrile of 81.2 %, so that the yield of acrylonitrile amounts to 75.3 %. 4.9 % of the propene introduced was, moreover, converted into carbon oxides.

WHAT WE CLAIM IS:—

1. A process for the preparation of ethylene nitriles by catalytic oxidation in the vapour phase of an olefin in the presence of ammonia, characterised by the fact that the use is made of a catalyst containing, in addition to oxygen, cobalt, iron, bismuth, tungsten, molybdenum, and optionally silicon, and also an element Z selected from group Ia or group IIa of the Periodic Table the proportions of these various elements being so selected that the atomic ratios are within the following ranges:

olefin, 1 to 10 volume % ammonia, 5-15 volume % molecular oxygen, 20-60 volume % water vapour, and 20-60 volume % of an inert gas, for example nitrogen, at a temperature between 250 and 500°C and under a total pressure close to atmospheric pressure, preferably between 1 and 2 bars. Suitable contact times are of the order of 1 to 10 seconds. The catalyst may be dis-

posed in a fixed bed, for example in a 10 multibar reactor, or in a fluidised bed.

By operating under the conditions thus described it is possible to obtain, for example with propene, practically quantitative conversion rates with a selectivity of 15 acrylonitrile higher than 80%.

The expressions—conversion, selectivity, and yield are defined as follows:

$$\text{Conversion \%} = \frac{\text{Number of moles of reacted olefin}}{\text{Number of moles of olefin introduced}} \times 100$$

$$\text{Selectivity \%} = \frac{\text{Number of moles of ethylene nitrile formed}}{\text{Number of moles of reacted olefin}} \times 100$$

$$\text{Yield \%} = \frac{\text{Number of moles of ethylene nitrile formed}}{\text{Number of moles of olefin introduced}} \times 100$$

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Co/Fe/Bi/W/Mo/Si/Z = 2.0-20.0 / 0.1-10.0 / 0.1-10.0 / 0.5-10.0 / 2-11.5 / 0-15.0 / 9.005-1.0 and the sum of the atomic ratios of molybdenum and tungsten is 12.

5 2. A process according to Claim 1 in which propylene is oxidised to form acrylonitrile.

3. A process according to Claim 1 in which isobutene is oxidised to form methacrylonitrile.

10 4. A process for the preparation of

ethylene nitriles substantially as hereinbefore described, with reference to Example 1 or Example 2.

5. An ethylene nitrile produced by the process of any of Claims 1 to 4.

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