Chemistry

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Abstract

Full Text

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ON THE PROCESS OF OBTAINING METHACRYLIC ACID NITRILE BY OXIDATIVE AMMONOLYSIS OF ISOBUTYLENE WITH AIR OXYGEN

At present, the synthesis of methacrylic acid nitrile (MAN)* both in the Soviet Union and abroad is carried out by a two-stage method via the nitrile of α-hydroxyisobutyric acid. The starting nitrile of α-hydroxyisobutyric acid is obtained from acetone and hydrogen cyanide in the presence of alkaline catalysts ([1]-[2]).

[Figure 1]

Fig. 1. Yield of MAN as a function of temperature. $T = 3$ sec.
$C_4H_8 : NH_3 : O_2 : H_2O = 1 : 2 : 2.5 : (1\text{–}3)$

In 1960 patent data were published ([3],[4]) on obtaining methacrylic acid nitrile by the method of oxidative ammonolysis of isobutylene in the presence of air oxygen. According to these data, the yield of methacrylic acid nitrile does not exceed 12%, calculated on the starting isobutylene. There is also another method for obtaining methacrylonitrile by ammonolysis of methacrolein ([5]), in which the yield of the target product amounts to 22% of the starting methacrolein.

Several works have been published ([6],[7]) devoted to obtaining methacrolein by oxidation of isobutylene.

Continuing the study of the oxidative ammonolysis of propylene ([8]), begun in 1962, we investigated the process of obtaining methacrylic acid nitrile by the method of oxidative ammonolysis of isobutylene in the presence of air oxygen. The experiments were carried out on laboratory installations in flow-type reactors, with fixed and fluidized beds of catalyst. The nitriles obtained in this process were analyzed by chemical and chromatographic methods.

[Figure 2]

Fig. 2. Effect of the molar ratio of ammonia and isobutylene on the yield of MAN. $T = 3$ sec., $t = 420°$.
$C_4H_8 : O : H_2O = 1 : 2.5 : (1\text{–}3)$

The influence of the main process parameters—temperature, the molar ratio of the starting components, and contact time—on the yield

* MAN in the figures denotes methacrylic acid nitrile.

methacrylic acid nitrile. The effect of temperature on the process of oxidative ammonolysis of isobutylene was studied in the range 350–480°.

Figure 1 shows the dependence of the yields of methacrylic acid nitrile on the process temperature. As can be seen from it, at a temperature of 350–370° the formation of methacrylic acid nitrile is insignificant, although the conversion of isobutylene reaches 50%. At the same time, the yield of CO_2 is 50% based on converted isobutylene.

It should be noted that, with an increase in temperature to 420°, a sharp decrease in the yield of CO_2 is observed, with a simultaneous increase in the yield of methacrylic acid nitrile. At a temperature of 420–450° the yield of CO_2 stabilizes at a level of 15%.* This phenomenon is apparently associated with a more rapid increase in the rate of the ammonolysis reaction of methacrolein to methacrylonitrile as compared with the increase in the rate of oxidation of methacrolein to CO_2. A further increase in temperature (above 450°) leads to an increase in the conversion of isobutylene α-iso-C_4H_8 with a simultaneous decrease in the selectivity of the process. The maximum yield of methacrylic acid nitrile under the conditions studied occurs at a temperature of 420°.

Fig. 3. Dependence of the yield of products in the process of oxidative ammonolysis of *iso*-C_4H_8 on the molar ratio O_2 and *iso*-C_4H_8 at:
$t = 420°$, $NH_3 : C_4H_8 = 2 : 1$

The results of studying the influence of the molar ratio of the initial components are shown in Fig. 2. From this figure it is evident that the best yields of methacrylic acid nitrile occur at a molar ratio of ammonia to isobutylene of 2–3.0 : 1.

A decrease in the molar ratio of ammonia to isobutylene leads to a reduction in the yields of methacrylic acid nitrile owing to a proportional increase in CO_2, while an increase in the molar ratio of ammonia to isobutylene to about 2.9–4.4 : 1 somewhat decreases the yield of methacrylic acid nitrile.

In studying the effect of oxygen concentration on the process of oxidative ammonolysis of isobutylene, it was established that the overall degree of conversion of isobutylene and its conversion into methacrylic acid nitrile at a ratio of 3.0–2.5 moles of O_2 per 1 mole of isobutylene were, respectively, 80–85% and 60–65% (Fig. 3).

Fig. 4. Curves of the dependence of the yields of MAN, CH_3CN and HCN and CO_2 on contact time at
$t = 420°$, $C_4H_8 : NH_3 : O_2 : H_2O = 1 : 2 : 2.5 : (1\text{–}3)$

Next, the dependence of the yield of methacrylic acid nitrile on contact time in the range 1–6 sec was studied. The results of the experiments in this series are shown graphically in Fig. 4, from which it is evident that the maximum yield of methacrylic acid nitrile occurs at a contact time of 2.5–3 sec.

As a result of the work carried out, it was established that the highest yields of methacrylic acid nitrile are obtained at a temperature of 420°, with the molar ratio of the initial components of the process *iso*-C_4H_8 :

: NH_3 : O_2 : H_2O = 1 : 2 : 2.5 : (1-3) and a contact time of 3 sec. Under these conditions, the yield of methacrylonitrile is 55-60%, with a selectivity of 60–65% and an isobutylene conversion of 80–100%. In this process, 15–20% of nitriles with formic, acetic, and acrylic acids are obtained as by-products.

Methacrylonitrile was isolated from the products of oxidative ammonolysis in pure form by extractive distillation with water, followed by azeotropic drying.

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Note: Figure translations are in progress. See original paper for figures.