Chemistry

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Abstract

Full Text

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On the Process of Producing Acrylonitrile from Propylene and Ammonia

Until recently, there existed two methods for producing acrylonitrile: from ethylene oxide and hydrocyanic acid, and from acetylene and hydrocyanic acid. Comparatively recently, a number of other methods for producing acrylonitrile were developed that are of industrial interest and capable of competing with the previously known industrial methods^(1-4). However, the most promising is the one-stage process of direct synthesis of acrylonitrile from propylene and ammonia, developed by Standard Oil. Reports on this process first appeared in the literature in the second half of 1959^(5). Shortly before the appearance of this report, and independently of it, we also demonstrated the fundamental possibility of producing acrylonitrile by direct synthesis from propylene and ammonia in the presence of atmospheric oxygen.

On a catalyst consisting of oxides of metals of variable valence, work was carried out to study the kinetic regularities of the process of oxidative ammonolysis of propylene.

The experiments were conducted on a laboratory flow-type setup with a stationary catalyst bed. In the course of the work, the influence of catalyst grain size, temperature, and the ratio of the starting reagents was studied.

Table 1

Temp., °C	α-C_3H_6	α-AN
350	3	0
400	28	30
400	30	28
430	50	50
450	68	65
450	70	68
500	70	60
500	70	55

In studying the influence of catalyst grain size, it was shown that, at a grain

Figure 1 and Figure 2 graphs

Figure 1: Figure 1 and Figure 2 graphs

Figure 3 graph

Figure 2: Figure 3 graph

size of 0.2-1.5 mm, the reaction proceeds in the kinetic region. The influence of temperature on the oxidative ammonolysis of propylene was studied within the range 350-500°, at a contact time of 2 sec and with the ratios $C_3H_6 : NH_3 : O_{2\,\text{air}} : H_2O = 1 : 1 : 1.8 : 1$. The dependences thereby obtained of the overall degree of conversion of propylene (α-C_3H_6) and of the conversion of C_3H_6 to acrylonitrile (α-AN) on temperature are presented in Table 1.

As is seen from the data of Table 1, at a temperature of 350° formation of acrylonitrile is not observed. A further increase in temperature leads to an increase in propylene conversion and selectivity. The maximum yield of acrylonitrile is reached at 450-470°; at higher temperatures the yield of acrylonitrile decreases, possibly owing to the formation of by-products. The influence of the ammonia and oxygen content in the initial mixture on the process of oxidative ammonolysis of propylene was also studied. The ammonia content in the initial mixture was varied within the range 0.3-1 mole of NH_3 per 1 mole of C_3H_6. The experimental results are presented in Fig. 1, from which it follows that the overall conversion of propylene does not depend on the concentration of ammonia in the initial feed. However, the conversion of propylene to acrylonitrile, when the ammonia content in the initial gas is lowered from 1 to 0.3 mole of NH_3 per 1 mole of C_3H_6, falls from 60-70% to 40% owing to an increase in the yield of acrolein to 17% and a slight increase in the yield of

CO_2. When the ammonia content in the initial feed is below 0.6 mole of NH_3 per 1 mole of C_3H_6, its conversion approaches 100%.

In studying the effect of the oxygen concentration on the process of oxidative ammonolysis of propylene, it was established that the overall degree of conversion

Fig. 1. Effect of the NH_3 content in the feed on the process of oxidative ammonolysis of propylene. $\tau = 2$ sec., $t = 450°$,
$C_3H_6 : O_2 : H_2O = 1 : 1.5 : 1$

Fig. 2. Effect of the C_3H_6 content in the feed on the process of oxidative ammonolysis of propylene. $\tau = 2$ sec., $t = 450°$, $C_3H_6 : NH_3 : H_2O = 1 : 1 : 1$

of propylene and the degree of its conversion to acrylonitrile, in the interval of $3 \div 1.5$ moles of O_2 per 1 mole of C_3H_6, remain unchanged and amount, respectively, to 70 and 60%. However, a further decrease in the oxygen content

Fig. 3. Dependence of the reaction rate on the concentration of propylene in

Figure 4. Dependence of the reaction rate constant on temperature. $\tau = 2$ sec., $t = 450^\circ$, $C_3H_6 : NH_3 : H_2O = 1 : 1 : 1$

Figure 3: Figure 4. Dependence of the reaction rate constant on temperature. $\tau = 2$ sec., $t = 450^\circ$, $C_3H_6 : NH_3 : H_2O = 1 : 1 : 1$

the initial mixture

in the initial gas mixture causes a sharp drop in conversion and selectivity (Fig. 2). This can probably be explained by the fact that, when there is a deficiency

oxygen in the feed gas, oxygen that is part of the catalyst begins to enter into the reaction, which leads to a change in the composition of the catalyst oxides and to a sharp drop in its activity. In connection with this, the oxygen content in the initial mixture must be not less than 1.5 moles of O_2 per 1 mole of C_3H_6. A further increase in the oxygen content in the feed leads to a decrease in the concentration of propylene. Since in the process of oxidative ammonolysis of propylene the oxygen of air is used, the concentration of propylene changes quite substantially, which, other conditions being equal, leads to a significant change in the reaction rate.

Fig. 4. Dependence of the reaction rate constant on temperature. $\tau = 2$ sec., $t = 450^\circ$, $C_3H_6 : NH_3 : H_2O = 1 : 1 : 1$

Figure 3 presents the dependence of the reaction rate on the concentration of propylene in the initial mixture. As can be seen from Fig. 3, there is a linear relationship between the reaction rate and the propylene concentration, indicating that the oxidative ammonolysis of propylene is a first-order reaction with respect to propylene.

In view of the fact that the conversion of propylene does not depend on the concentration of oxygen and ammonia, the oxidative ammonolysis of propylene is a zero-order reaction with respect to oxygen and ammonia.

Thus, the rate of the oxidative ammonolysis reaction is described by the equation

$$W = KC_{C_3H_6},$$

where K is the reaction rate constant, and $C_{C_3H_6}$ is the concentration of propylene. The graphical dependence of $\lg K$ on reciprocal temperature is shown in Fig. 4. In the temperature range 350–475°, the activation energy of the overall reactions occurring in the synthesis of NAC is ~ 21000 cal/g-mole; at higher temperatures, diffusion limitations apparently arise.

On the basis of laboratory data, the currently operating pilot-plant unit was constructed.

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