INFLUENCE OF AMMONIA ON PROPANE OXIDATION OVER A GALLIUM-ANTIMONY OXIDE CATALYST

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The influence of ammonia on propane oxidation over a Ga-Sb oxide catalyst has been studied. Acrylonitrile is formed upon the interaction of acrolein with partially dehydrogenated ammonia. Ammonia increases the rates of overall and selective oxidation of propane. This is assumed to be due to the formation of electron-donor sites promoting proton separation from the propane molecule.

The interaction of propane and ammonia with oxygen on oxide catalysts has been little studied. On the basis of qualitative analysis of the products of propane ammoxidation the authors of Ref. /1/ suggest a scheme of propane conversion to acrylonitrile via intermediate formation of propylene and acrolein. The authors assume ammonia to participate in the transformation of acrolein to acrylonitrile as well as to prevent the decomposition of intermediate oxygen-containing compounds.

The present study was initiated to elucidate the influence of ammonia on propane oxidation over Ga-Sb containing catalysts.
Experiments were performed in a flow-circulation apparatus with a gradientless reactor supplied with a vibro-fluidized catalyst bed and a pulse installation with chromatographic product and reagent analysis.

A Ga-Sb oxide catalyst containing nickel and phosphorus with the atomic ratio Ga:Sb:Ni:P = 1:3:1.5:1 was prepared via precipitation with ammonia solution from a mixture of salt solutions by the procedure described in Ref. /2/. The specific catalyst surface measured by nitrogen adsorption was equal to 5.5 m$^2$/g. The influence of ammonia on propane oxidation was studied at constant concentrations of propane and oxygen equal to 5 and 18.6 vol%, respectively, and at ammonia concentrations varying from 0 to 0.2%. The reaction temperature was 550 °C and the contact time was varied from 5 to 25 sec.

Special experiments on homogeneous oxidation in an empty reactor show that the reaction proceeds heterogeneously.

I. Influence of ammonia on the composition of propane oxidation products.

The main products of propane oxidation over the Ga-Sb catalyst are acrolein, carbon monoxide and dioxide. The reaction products of propane ammoxidation also involve acrylonitrile and small amounts of acetonitrile and prussic acid. When 0.03% ammonia is introduced into the mixture (Fig. 1) acrylonitrile appears as a product. With increasing ammonia concentration, the selectivity to acrylonitrile rises, while that to acrolein decreases. With 2% ammonia in the reaction mixture, acrolein disappears from the products. On the basis of these data it may be concluded that acrylonitrile is formed from acrolein upon its interaction with ammonia. The formation of extensive oxidation products is mainly due to further oxidation of acrolein and acrylonitrile as is seen in Fig. 1 (0.20% NH$_3$).

II. Forms of ammonia participating in the reaction.

By analogy to propylene /3/, it may be assumed that the formation of acrylonitrile involves adsorbed ammonia. To elucidate this assumption, experiments were made in a pulse installation. After passing 1% ammonia pulses over a catalyst, 3