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Abstract

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HYDROCHLORINATION OF ACETYLENE ON ALUMINUM OXIDE IN A FLOW SYSTEM

(Presented by Academician S. I. Volʹfkovich, 18 VII 1957)

Acetylene, possessing very high reactivity, adds hydrogen chloride with the formation of vinyl chloride. The latter, as is known, is readily polymerized and copolymerized into plastic products.

At present, the principal starting materials for obtaining vinyl chloride in industry are dichloroethane and acetylene. Accordingly, industry operates by two main methods (^{1}-^{5}). The method of dehydrochlorination of dichloroethane with an alcoholic solution of alkali has entered industrial practice and still remains of great importance; this method is used in the USA.

The second important method for producing vinyl chloride, used in Germany, is the addition of hydrogen chloride to acetylene. This reaction is carried out either in the gas phase or in a liquid medium. When the reaction is carried out in the gas phase, the catalyst is mercuric chloride on porous supports. When the reaction is carried out in a liquid medium, cuprous chloride is used.

The most economically advantageous method for obtaining vinyl chloride is the first method. However, the considerable inconveniences encountered in working with mercury catalysts are prompting researchers to seek economical mercury-free catalysts.

The present communication sets forth data from a laboratory investigation on the use of aluminum oxide in the hydrochlorination of acetylene.

Vinyl chloride was obtained by the authors from acetylene and hydrogen chloride over aluminum oxide by a flow method in the temperature range 250–350°. The reaction of addition of hydrogen chloride to acetylene was studied as a function of the following parameters: 1) preliminary treatment of the catalyst with hydrogen chloride, 2) the dosage of hydrogen chloride in the initial gas mixture, and 3) temperature.

The experiments on the hydrochlorination of acetylene were carried out in an ordinary flow-type apparatus with industrial aluminum oxide. Acetylene and hydrogen chloride, previously purified and dried, passed through a mixer into a catalytic furnace.

The gas mixture after the reactor, consisting of the vinyl chloride formed and unreacted acetylene, was collected in a gasometer of the Patrikeev system with an automatic pressure regulator. The third component—hydrogen chloride—was absorbed along the way by water. The content of vinyl chloride in the gas mixture was determined from the molecular weight and recalculated to percentage composition, which corresponded to the yield of vinyl chloride based on acetylene.

In doing so, it was borne in mind that, simultaneously with the hydrochlorination reaction, partial decomposition of acetylene into carbon and hydrogen occurs, accompanied by carbon deposition on the catalyst, which was taken into account

during regeneration of the catalyst with CO_2. Hydrogen was detected in the gas mixture, but in considerably smaller amounts than those calculated from carbon deposition. Therefore, the yield of vinyl chloride was determined, as indicated above, from a two-component system: acetylene—vinyl chloride*.

In carrying out the experiments it was shown that the yield of vinyl chloride depends substantially on the preliminary treatment of the catalyst with hydrogen chloride and on the conditions under which this treatment is carried out. Table 1 summarizes

Table 1

Experiment No.	Treatment of Al_2O_3 with HCl gas: duration, h	Treatment of Al_2O_3 with HCl gas: temp. in reactor, °C	Molecular weight of the gas mixture obtained	Yield of vinyl chloride, % relative to acetylene	Carbon deposition, % relative to acetylene
1	Without preliminary treatment	Without preliminary treatment	41.44	42.3	10.6
3	9	20	43.63	48.3	9.1
5	7	300	40.70	40.3	Not counted
19 (repeat)	3	200—300	47.56	59.1	9.1

experiments: a) without preliminary treatment of the catalyst with hydrogen chloride (experiment 1); b) with preliminary passage of hydrogen chloride at room temperature for 9 h, followed by raising the temperature to the reaction temperature (experiment 3); c) the same, with simultaneous raising of the temperature from room temperature to 300° over 3 h (experiment 19).

Table 2

Experiment No.	Acetylene: hydrogen chloride	HCl in the initial gas mixture, %	Molecular weight of the gas mixture obtained	Yield of vinyl chloride, % relative to acetylene	Carbon deposition, % relative to acetylene	HCl removed from the catalyst after the reaction, ml per 1 g catalyst
8	1 : 0.60	37.5	39.21	36.2	11.0	4.2
7	1 : 1	50.0	42.13	44.2	Not counted	8.1
19	1 : 1.25	55.5	47.56	59.1	9.1	12.9
9	1 : 1.85	65.0	48.29	61.1	Not counted	31.6
12	1 : 2.60	72.0	48.92	62.8	3.7	118.5

The experiments were carried out at 300°; the catalyst charge was 50 ml (bulk density 0.53 g/ml). Acetylene was fed into the reactor at a rate of 2.1 l/h, and hydrogen chloride at a rate of 2.3–2.4 l/h.

It is seen from Table 1 that, with preliminary treatment of the catalyst with hydrogen chloride, the yield of vinyl chloride increases to 59% when the catalyst is pretreated for three hours with simultaneous heating of the reactor to the reaction temperature.

The influence of the dosage of hydrogen chloride in the initial gas mixture on the formation of vinyl chloride was studied at acetylene-to-hydrogen chloride ratios ranging from 1 : 0.6 to 1 : 2.6.

The results of the experiments are given in Table 2.

It is seen from Table 2 that, with a slight excess of hydrogen chloride (5.5%, experiment 19) over the stoichiometric ratio in the initial gas the yield of vinyl chloride increases sharply (59.1%). With an approximately fourfold increase in the excess of HCl (22%, experiment 12), no further significant increase in the yield of vinyl chloride is observed (62.8%).

* In most experiments, formation of up to 0.5 ml of liquid products was observed, condensing in two layers. The lower layer corresponded to a 10–15% HCl solution, and the upper layer to a mixture of acetylene chloro-derivatives. These products were not studied in detail and were not taken into account because of their small quantity.

Fig. 1

Figure 1: Fig. 1

In the indicated experiments, the amount of hydrogen chloride removed from the catalyst after the reaction was taken into account: as is seen from Table 2, the yield of vinyl chloride depends to some extent on the amount of HCl that remained adsorbed during the reaction and was then removed by purging. Also of interest is the observed progressive increase in the amount of HCl on the catalyst with an increase in the gas feed in the initial mixture; moreover, it has no substantial effect on increasing the yield of vinyl chloride.

Fig. 1

Owing to the exothermic nature of the reaction of hydrochlorination of acetylene to vinyl chloride, the choice of temperature regime is important. According to thermodynamic calculations carried out by the authors on the basis of literature data (([6],7)), the equilibrium of the hydrochlorination reaction of acetylene at room temperature is completely shifted toward the formation of vinyl chloride. With increasing temperature, owing to the exothermicity of the process, the equilibrium shifts to the left. However, in the range (250–350^{ }) the equilibrium constant is still sufficiently large and changes from (3 10^4) to (4.6 10^2). In this temperature range we studied the dependence of vinyl chloride formation on temperature (see Fig. 1, 1); data were also obtained on the change in the amount of carbon deposition in the same temperature range (Fig. 1).

As is seen from Fig. 1, the yield of vinyl chloride increases with temperature, and the maximum yield ((70%)) lies within (300–320^{ }). At (350^{ }) the yield is lower than at (300^{ }). In these experiments acetylene was fed at a rate of 1.9-2.1 and 4.1 l/hour (at (320^{ })); the ratio of acetylene to hydrogen chloride was (1 : 1.25). Under these parameters the activity of the catalyst did not change over 4 hours, which is sufficient for kinetic studies of the process, which are currently being carried out.

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