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DESCRIPTION OF THE INDUSTRIAL PROCESS ETHYLENE ACETOXYLATION

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Annotation: The article is devoted to the essence of the acetoxylation process. The types of the process, their main differences, the advantages of each are considered. The corresponding reactions, conditions, catalysts, mechanisms and production stages are given. The main reaction products are described and characterized: vinyl acetate and ethylene glycol.

Key words: acetoxylation, vinyl acetate, ethylene, ethylene glycol.

The acetoxylation process is the addition of an acetoxy group to a chemical compound or the reaction of oxidative coupling of alkenes. In the second half of the twentieth century, the use of these reactions in industry "gained popularity." Acetoxylation of ethylene to produce vinyl acetate, ethylene glycol monoacetate, butylene glycol diacetate, etc. has become especially useful.

The main task of this industrial process is to obtain vinyl acetate as a very valuable material in the production of polymers and copolymers. The reaction for obtaining this substance was discovered and developed by I.I. Moiseev. It was based on the oxidative combination of ethylene with acetic acid. Initially, acetylene was used in the industrial method for producing vinyl acetate, but with the advent of acetoxylation on a palladium catalyst, the technology was changed, and ethylene became the main raw material. At the moment, more than 90% of vinyl acetate is produced using this technology.

There are two main methods for producing vinyl acetate: liquid phase and gas phase.

The liquid phase method was the first breakthrough in vinyl acetate production. It was carried out with the participation of a palladium catalyst, but in an acidic rather than aqueous medium, which allowed the intermediate carbocation CH_3-CH-OCO-CH_3 to detach a proton and form vinyl acetate. When carrying out a liquid-phase process, a $PdCl_2$-$CuCl_2$ catalyst (sometimes with the addition of iron) in acetic acid with the addition of CH_3COONa or LiCl is used. The addition of alkali metal acetates (about 5 wt%) increases the efficiency of the Pd catalyst by a factor of 10. There is also a method of catalysis with a heterogeneous bimetallic catalyst Pd-Au (fine gold or in the composition of a salt).

By-products are: n-butene, due to ethylene dimerization; acetaldehyde; carbon dioxide; acids, esters.

$$CH_2 = CH_2 + CH_3COOH + 0{,}5O_2 \rightarrow CH_2 = CHOCOCH_3$$

The process takes place under the following conditions: temperature about 110 degrees Celsius, pressure 3-4 MPa, Pd content 40 mg / l, Cu 4 g / l. The water that forms during the reaction increases the yield of aldehyde.

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As a result, the process has a low yield of the required product, and the equipment is subject to severe corrosion. That is why, at the moment, the gas-phase process is considered more perfect.

In the Soviet Union, the gas-phase acetoxylation method was carried out for the first time in 1976. A heterogeneous catalyst is used, which includes palladium supported on a porous support, alkali metals and metals of variable valence (most often Cu). For example, the palladium-bismuth-potting composition Pd-Bi-K contributes to an increase in the selectivity and efficiency of the catalyst. Al_2O_3, SiO_2, hydrothermally treated silica support and activated carbon are used as the support. The carrier motivates the oxidation of Pd to the bivalent form:

$$Pd + 0{,}5O_2 + 2CH_3 - COOH \rightarrow P$$
$$Pd^{2+} + CH_2 = CH_2 + CH_3COOH \rightarrow$$
$$= CH - OCO - CH_3 + 2$$

Reaction conditions: temperature 175 degrees Celsius, pressure 0.5-1 MPa. To prevent an explosion, excess ethylene and acetic acid are present in the mixture passed through the palladium catalyst. This excess goes to new oxidation; therefore, it is necessary to use oxygen as an oxidizing agent, not air. The initial volume ratio of the components should be 8 (ethylene): 4 (acetic acid vapor): 1 (oxygen). As a result, the yield of vinyl acetate reaches 92%; the products also contain carbon dioxide and about 1% of other products, mainly acetates [1].

As mentioned above, ethylene acetoxylation proceeds on palladium catalysts. The corresponding stoichiometric reaction can be written as follows:

$$CH_2 = CH_2 + PdCl_2 + 2CH_3COONa \rightarrow CH_2$$
$$= CHOCOCH_3 + 2NaCl + Pd^0 + CH_3COOH$$

A π-complex is formed, which attacks, like a nucleophile, the acetate ligand. After that, the hydrogen proton is split off and the acetate ligand is attached. Pdisreducedfromvalency +2 to 0.

If the reaction is catalyzed by an active dimer of palladium acetate (in glacial acid), then the next step will be the addition of ethylene either to the adjacent terminal acetate molecule, or this addition will occur to the acetate from the solvent. In the subsequent stages, ligands co-operate with acetate ions and the hydrogen atom migrates. The last stage is the rate-limiting stage, which occurs with the displacement of hydrogen, the so-called hydride shift.

The figure shows a technological scheme for the production of vinyl acetate:

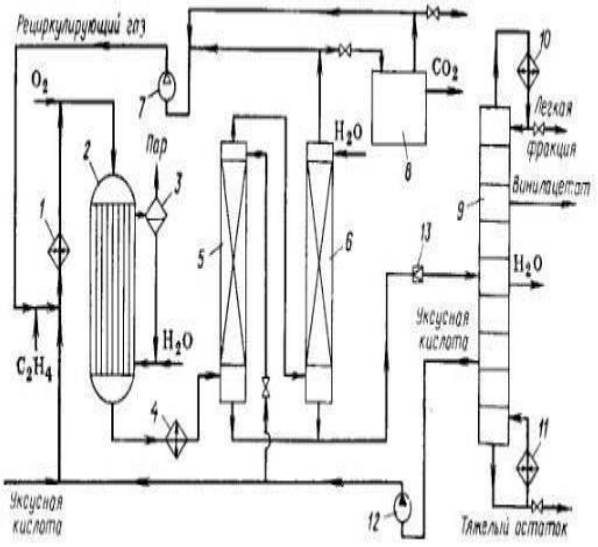

Figure 1. Technological scheme for the production of vinyl acetate from ethylene

The scheme shows the industrial synthesis of vinyl acetate from ethylene. 1 mixture of acetic acid and ethylene is heated to a certain temperature in a steam heater. 2 - then the resulting mixture is combined with oxygen and sent to a tubular contact apparatus with a stationary layer of a paladium catalyst located in the pipes. 3- due to the evaporation of water condensate, the released heat is removed, also the simultaneously generated steam is separated

in the collector. 4- the reaction mixture is cooled in a refrigerator. 5-6 flush the gas with acetic acid and water sequentially in scrubbers for the extraction of vinyl acetate and acetic acid. 7- most of the scrubbed gas is returned by the circulating compressor to synthesis, part of it passes through block 8 for carbonate purification from carbon dioxide. The cleaned gas is partially recirculated, but some is removed from the system to avoid a large accumulation of inert impurities contained in ethylene and oxygen. The mixture of liquid products from the cube of scrubbers 5 and 6 is sent for separation to the system of rectification columns 9, where vinyl acetate, water, acetic acid and heavy impurities are separated and sent for combustion.

Industrial acetoxylation has been developing for half a century. His methods and catalysts are improving. We have considered the most important aspects of this process. Special attention was paid to the products as they are an important and valuable raw material in various industries. The acetoxylation method is in demand on the market mainly due to the low price of ethylene and acetic acid. However, it has two main drawbacks: high conversion requirement and explosiveness. Therefore, it is necessary to follow the path of improving the process and increasing production safety.

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