Selection of an effective catalyst for the stage isoamyl alcohol dehydration during synthesis isoprene from isopentane

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Abstract. The annual growth in the consumption of isoprene rubbers dictates manufacturers to searching for the new methods of its production. An intermediate product in the production of isoprene rubbers is the synthesis of a monomer - isoprene. The main industrial methods for its production in Russia are synthesis processes from isobutylene and formaldehyde and two-stage dehydrogenation of isopentane. The article analyzes and selects an effective catalyst for the stage of isoamyl alcohol dehydration in the synthesis of isoprene from isopentane.

Synthetic rubbers are in demand every year all over the world, thanks to the ability to regulate their performance properties.

The cost of obtaining them is approximately 25 to 30% of their cost price, which indicates the feasibility of their multi-tonnage production. Thus, all scientific research is aimed at improving this technology, which consists either in the production of a high-quality product using a low-cost technology, or from cheap and affordable raw materials, or using a waste-free method of production.

Large-tonnage production of 2-methylbutadiene-1,3 began in 1959 the company "Shell" in TORRANCE (USA), which consists in the allocation of isoamylene fraction of oil, followed by catalytic dehydrogenation in his 2-methylbutadiene is 1.3.

Currently, in Russia, is still common processes monomer is a way of getting from 2-methylbutanol and matamala and catalytic dehydrogenation of 2-methylpentane in two stages.

the main industrial methods of its production are the processes of synthesis from isobutylene and formaldehyde and two-stage dehydrogenation of isopentane. Separation from the pyrolysis fraction gives low productivity for the finished product. Therefore, the search for effective methods for obtaining a valuable monomer in the world practice remains an urgent task for any production of synthetic rubbers of various brands.

It is worth noting that the existing methods for producing isoprene have not changed in the last fifty years, these are the production of 2-methylpropene and formic aldehyde, extraction from pyrolysis fractions of oil, catalytic dehydrogenation of isobutylene in one stage, the method of ethine and primary propyl alcohol, and two-stage dehydrogenation of the pentane isomer.

The paper studies the liquid-phase method of synthesis of 2-methylbutaiene-1,3 by oxidative dehydrogenation of an isopentane-isoamylene mixture, as well as the one-stage method, where the raw materials are diluted with steam and hydrogen, the method of condensation of betenes with synthesis gas, accompanied by further decomposition of 2-methylbutanal. For the first time, various brands of
catalysts for the dehydration of tertiary alcohols obtained by domestic and imported manufacturers were tested.

Despite the advantages described above, the technology using iron-potassium contacts is expensive and energy-intensive. To make the technology less expensive, it is necessary to increase the degree of conversion of methylbutenes and selectivity for isoprene. This technology requires continuous improvement in order to reduce the cost of isoprene in a competitive market. However, the control levers of this technology are almost exhausted, and isoprene synthesized by the two-stage dehydration of isopentane has the highest cost. Therefore, the development of less energy-intensive technologies for the production of isoprene is a key task of Russian researchers. Of particular interest to scientists is the process of epoxidation of isobutylene. The advantage of the method: cost-effective, liquid-phase and implemented at moderate temperatures. The dehydration stage of this technology is intended for the production of isoamylene from isoamyl alcohol, which is formed in the epoxidation stage as a by-product. Two-stage catalytic dehydrogenation of 2-methylbutane is a domestic method. It is widely known and implemented in Russia [1,2]. Process conditions are: temperature from 570 to 630 °C, ratio C5-fraction: water vapor = 1: 20, oxide iron-potassium contact, self-regenerating [3,4].

Software materials are widely used for dehydrogenation processes in the modern world, in particular, products of mathematical modeling of dehydrogenation reactions, which make it possible to select the process conditions that ensure high conversions and selectivity of the formation of reaction products [5,6].

After having studied the regularities of the chemical transformations of the catalytic dehydrogenation process [7,8], it was identified that they are of a qualitative nature.

Based on the results of processing the literature data, it can be noted that one of the promising directions for the production of isoprene monomer is the method of epoxidation of 2-methylbutene-2 with the production of 2-methyl-2,3-epoxybutane followed by its dehydration into isoprene. in the epoxidation stage, in addition to 2-methyl-2,3-epoxybutane, tertiary amyl alcohol is formed. The qualified method of using a by-product - tertiary amyl alcohol (TAS) by converting it into the main raw material - 2-methylbutene-2. It makes this method even more attractive. Therefore, in this work, we study the possibility of carrying out the process of dehydration of tertiary amyl alcohol into 2-methylbutene-2 with the latter returning to the epoxidation stage.

Thus, this scientific work is based on the searching and selection of an effective catalyst for the dehydration of isoamyl alcohol and laboratory tests of selected catalyst samples in the process of TAS dehydration.

We selected inorganic acids and ion-exchange resins as catalysts for this process. Currently, well-known manufacturers of catalysts based on ion exchange resins are:

- Lewatit (Levatite).
- Amberlite (Amberlite).
- Purolite.
- Dowex (Davex).
- Tulsion (Tulsion).
- Relite.
- Resinex (Rezinex).
- With a smaller assortment: Bybron, Diaion, Granion, Jacobi, Polyion, Resindion, Resintech, Trilite.

Domestic producers of cation exchangers are OOO PO Tokem (Kemerovo), catalysts - OOO PKF Polyplast (Ishimbay), ZAO RTN (St. Petersburg).

To study the initial characteristics and tests, cation exchangers with a macroporous structure were selected: "Pyurolyte", T-103, T-103W (MTBE), Resinex, T-8052MP and the domestic catalyst KU-2-8.
The most effective brands were identified by laboratory tests in the dehydration of tertiary amyl alcohol using the catalysts and cation exchangers proposed above based on ion-exchange resins.

### Table 1. Characteristics of cation exchangers.

| Nameindicators | CCationite K "Pyurolyte" | CCationite TT-103 | CCationite TT-103W (MTBE) | CCationite RResinex | CCationite T-8052MP | Catalyst KU-2-8 |
|----------------|--------------------------|-------------------|---------------------------|---------------------|---------------------|-----------------|
| Manufacturer   | GGreat Britain |
|                 | PPO «Tokem» LLC | PPO «Tokem» LLC | JJacobi Carbons | TTulsion | RTN CJSC |
| Appearance     | Spherical grains up to 1.3 mm | Granules |
| Mass fraction of moisture, % | 556.3 | 662.2 | 555.5 | 558.8 | 554.4 | 54.4 |
| Catalytic activity (TAS conversion), % | 994.4 | 996.0 | 994.8 | 882.7 | 990.5 | 886.1 |
| Full static exchange load, (PSOE), -mmol / g; | 55.3 | 55.6 | 55.6 | 55.1 | 55.7 | 33.9 |
| - mol / l Mass fraction of free acid in terms of sulfuric acid, % | 11.7 | 0.5 | 22.0 | 11.8 | 22.0 | 11.1 |
| Specific volume, cm³ / g | 00.2 | 00.2 | 00.9 | 00.3 | 00.3 | 00.5 |
| Bulk density, g / cm³ | 33.1 | 110.5 | 22.8 | 22.8 | 22.8 | 33.5 |
| 00.78 | 00.25 | 00.81 | 00.86 | 00.78 | 00.62 |

In terms of activity indicators, the catalysts can be arranged in descending order of T-103, T-103W, Pyurolyte, T-8052MR, KU-2-8, Resinex.

As you can see in table 1, the T-103 cation exchanger differs from other samples in its high specific volume (highly swellable), which makes it not very attractive for use in an industrial reactor. When loaded into an industrial reactor, the mass of the cation exchanger (in terms of dry weight) will be less.

The highest value of PSOE of the studied cation exchangers in terms of mol / l was shown by the samples T-103W (MTBE) produced by OOO PO Tokem and the cation exchanger T-8052MP produced by Tulsion.

To carry out the process of dehydration of tertiary amyl alcohol into 2-methylbutene-2, the "Pyurolyte" catalysts and the domestic cation exchanger of the T brand are effective and technological.

During the experiment, the total static exchange capacity was calculated and measured by titrimetric determination of the concentration of sulfogroups-SO3H in the catalyst.

The essence of this method is to determine the amount of sodium ions absorbed from a solution of sodium hydroxide by a catalyst in contact with a constant volume of alkali.

The amount of sodium ions absorbed by the catalyst is determined by the difference in the concentrations of the alkali solution before and after contact with the catalyst. The concentration of the NaOH solution is determined by volumetric titration with an acid solution in the presence of an indicator.

In addition, the catalytic activity of the catalyst was determined, which was evaluated by the degree of dehydration of tert-amyl alcohol (TAC) under static conditions at the boiling point of the TAC - water azeotrope (at atmospheric pressure), measuring the amount of 2-MB-2 released during dehydration.
Thus, we have tested the selected catalysts and selected the most effective sample. Based on the analysis of scientific literature, as well as experimentally obtained data, the following conclusions can be drawn:

- T-103 cationite differs from other samples by its high specific volume (highly swellable), which makes it unattractive for use in an industrial reactor. When loaded into an industrial reactor, the mass of the cationite (in terms of dry weight) will be less.
- the highest value of the PSOE of the studied cationites in terms of mol/l was shown by the samples T-103W (MTBE) produced by LLC PO "Tokem" and T-8052MR cationite produced by Tulsion.
- for the process of dehydration of tertiary amyl alcohol in 2-mutilbutene-2, the catalysts "Purolite" and domestic cationite of the T-103W brand (MTBE) produced by LLC PO "Tokem" in Kemerovo are effective and technologically advanced.
- the domestic catalyst in terms of quality is not inferior to the imported analogue of the Purolite brand, for the industrial implementation of the process, the use of a domestic catalyst of the T-103W brand (MTBE) is recommended.

References

[1] Pavlov S Yu and Surovtsev A A 1997 Prospects for the development of production of isoprene and polyisoprene rubber Chemical industry 7 219
[2] Ogorodnikov S K and Idris G S 1973 Production of isoprene (Leningrad: Chemistry) 296
[3] Gilmutdinov N R, Hafizov A V, Korshunov A I et al. 1996 Oil refining and petrochemistry 9 29
[4] Aminova J I and Bazhenov Yu P 1998 Industry SK 1 S Z
[5] Slinko M G 1999 Principles and methods of technology of catalytic processes Teor. fundamentals of Chemical Technology ZZ(5) 528-38
[6] Slinko M G 2000 Scientific foundations of the theory of catalytic processes and reactors 41(6) 933-46
[7] Balandin A A, Bogdanova O K and Shcheglova A P 1965 Obtaining isoprene by catalytic dehydrogenation of isopentanes AN SSSR 162 1320-2
[8] Bogdanova O K, Shcheglova A P and Balandin A A 1959 Catalytic dehydrogenation of isopentane-isopentene mixtures Izvestiya AN SSSR. Otd. Chemical sciences 2 350-2