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Novel Ecological and Energy Saving Method of Single-Stage Synthesis of Isoprene

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Abstract

The possibility of single-stage synthesis of isoprene from 1,3,5-trioxane and trimethylcarbinol in the presence of heterogeneous catalyst – strongly acidic macroporous cation-exchange resin – was established. The composition of the reaction mixture was determined by means of gas-liquid chromatography. Along with isoprene, unreacted trimethylcarbinol was detected, as well as by-products: unsaturated isoamylenic alcohols and 4,4-dimethyldioxane-1,3 – precursors of isoprene; the formation of an additional amount of isoprene during the decomposition of these compounds is possible. Optimal process conditions were chosen, providing the degree of trioxane conversion up to 99 %, selectivity of the process with respect to isoprene 65 %, and the yield of isoprene per transformed trioxane 64 %. In comparison with the existing two-stage methods of isoprene synthesis from the aqueous solution of formaldehyde and isobutylene, the proposed method allows one to decrease energy consumption and diminish the amount of waste water due to the “soft” technological conditions of the process.

Key words: isoprene, trimethylcarbinol, 1,3,5-trioxane, cation-exchange resin, isobutylene, formaldehyde, energy saving

INTRODUCTION

During the recent two decades, the world demand for isoprene increased to such an extent that this compound became one of the most important exported products of Russian petroleum chemistry, with the cost much exceeding that of the ready isoprene caoutchouc. This is due to several factors, the major one being the appearance of the new grades of synthetic caoutchouc on the world market; the major raw material to obtain them is isoprene [1].

At present, isoprene is obtained at the territory of Russia mainly through a two-stage synthesis from isobutylene or trimethylcarbinol and 37–40 % aqueous solution of formaldehyde – formalin (the so-called dioxane method used at the Tolyattikauchuk Ltd., and the direct synthesis of isoprene realized at the Nizhnekamskneftekhim JSC [2–11]). The use of formalin

is due to the complicity of storage and transportation of highly concentrated formaldehyde. At the same time, the use of formalin in the system results in the formation of a large amount of ballast water directly participating in the formation of side products. As a consequence, the necessity to concentrate diluted formaldehyde solutions arises, which increases the energy consumption in the process and becomes the reason of the formation of large amounts of waste water.

Realization of isoprene synthesis in the system composed of two phases requires efficient and uniform mixing of reaction mixture, which also causes an increase in energy consumption, the appearance of a large number of side products and, as a consequence, an increase in the net cost of isoprene.

In this connection, the search for new efficient methods of isoprene synthesis, including

the procedures that involve anhydrous formaldehyde or its derivatives as one of the initial reagents, is of substantial scientific interest. One of these reagents may be 1,3,5-trioxane – a cyclic trimer of formaldehyde which has not been used for this synthesis before.

In the existing methods of isoprene synthesis, usual catalysts are liquid organic acids (oxalic, oxyethylidenediphosphonic) and inorganic ones (orthophosphoric, sulphuric). At the Tolyattikauchuk JSC, solid acid (calcium phosphate or calcium borophosphate) catalysts are used at the second stage of synthesis for splitting 4,4-dimethyldioxane-1,3 to isoprene [2].

Disadvantages of liquid acid catalysts include their high corrosion activity (especially sulphuric acid) and the necessity to neutralize the catalyst after the synthesis, which causes an increase in the net cost of isoprene due to the use of equipment made of special doped alloys and due to the formation of large amounts of waste water. At the same time, this kind of catalysts is distinguished by relatively low cost and simplicity of application.

Calcium phosphate and calcium borophosphate catalysts have low selectivity of dimethyldioxane decomposition, high working temperature (above 300 °C) and a short period of catalytic activity. They require high consumption of water vapour as a diluent of the reaction mass and for catalyst recuperation, which enhances energy consumption for synthesis and promotes the formation of waste water and recycle flows in large amounts [2, 12].

To exclude all the mentioned disadvantages, it is proposed to use strongly acidic macroporous ion exchange resin of Granion D 001 grade as the catalyst in the new method of synthesis. This resin is characterized by the high ion exchange capacity, wear resistance and swelling strength; it also has several advantages over homogeneous catalysts and over some heterogeneous acid catalysts.

The major advantages of its use are low corrosive aggressiveness of the resin towards the equipment, the absence of the necessity to neutralize the catalyst after the synthesis, low temperature of the manifestation of the maximal activity and the possibility of multiple use of ion exchange resin without any noticeable decrease in its catalytic activity [13, 14].

EXPERIMENTAL

Initial reagents for this method of isoprene synthesis are the following compounds:

1. 1,3,5-Trioxane – cyclic anhydrous trimer of formaldehyde. Pure compound content 99.5 mass %, $T_m = 61\text{--}62\text{ }^{\circ}\text{C}$, $T_b = 115\text{ }^{\circ}\text{C}$. Colourless crystal substance, easily sublimable, soluble in water, alcohols, ketones, organic acids, esters, aromatic hydrocarbons, easily decomposes to form formaldehyde in the acidic medium.

2. Trimethylcarbinol – tertiary butyl alcohol (TU 6-09-4297-76). The major compound content 88 mass %, $T_m = 25.5\text{ }^{\circ}\text{C}$, $T_b = 82.9\text{ }^{\circ}\text{C}$; $d_4^{20} = 0.805\text{ g/cm}^3$; $n_D = 1.3954$. Colourless liquid, infinitely soluble in water forming an azeotrope with it, well soluble in organic solvents. When heated in acidic medium to 110 °C and higher temperature, decomposes to form isobutylene and water.

3. Cation-exchange resin of Granion D 001 grade – strongly acidic macroporous cation-exchange resin of industrial and food classes on the basis of the sulphurized copolymer of styrene and divinylbenzene. It possesses high chemical and thermal stability, high mechanical strength and low sensitivity to high-molecular mass organic contamination; it conserves high exchange capacity within a broad pH range. Total static exchange capacity is equal to 5.0 mg-equiv./g, moisture content is 50–55 %, maximal operation temperature 120 °C.

Isoprene synthesis is carried out in an autoclave reactor, which is a metal vessel 300 cm³ in volume, equipped with a case, sampling device, manometer and a mixer. Triethylene glycol is used as a heat carrier. The volume of the reaction mixture is 100–200 cm³.

To study the dependence of isoprene yield, the molar ratio of trioxane to methylcarbinol was varied from 1 : 4.5 to 1 : 18, the amount of cation-exchange resin was varied from 2.5 to 20 mass % [15].

In the beginning of the synthesis, calculated amounts of 1,3,5-trioxane, trimethylcarbinol and the catalyst (cation-exchange resin) are placed into the reactor. Then the reactor is tightly closed, thermostat is switched on to supply heat carrier with preset temperature, and the mixing device is switched on. The moment

when the reaction mixture reaches the temperature differing from the preset value (120 °C) by not more than 1 °C is accepted as the start of the reaction. Reaction time is 150 min.

In the course of reaction, samples up to 0.5 mL in volume are taken after definite time intervals. After the synthesis is over, the mixing device is switched off; cool water is supplied to the autoclave case for 20–30 min to cool the reaction mixture to 10–15 °C. Then the reaction mass is discharged into a glass stoppered flask which is cooled with water and ice.

Analysis of reaction products is performed with KristallYuks 4000M chromatograph with the flame ionisation detector (FID).

Procedure of gas chromatographic analysis

Analysis of the composition of reaction mixture is carried out under the following conditions: liquid phase – pentaerythrite tetrabutyrate in the amount of 15 % of the mass of solid support, solid support – diatomite brick, carrier gas – helium, column length – 100 m, column diameter – 0.3 mm. Chromatograph operation mode: evaporator temperature 250 °C, detector temperature 270 °C, column temperature 40 °C, carrier gas flow rate 20 cm³/min, volume of sample introduced into the chromatograph 0.5 µL.

Calculation of chromatograms and identification of reaction products are performed automatically with the help of the computer programme NetChrom v2.1 by means of internal normalization.

Determination of free formaldehyde content and unreacted trioxane is carried out by means of oxymation.

Procedure of titrimetric determination of formaldehyde (oxymation method)

Two conical flasks, each of them 250 mL in volume, are charged with 50 mL of 0.5 M hydroxylamine hydrochloride solution, then six drops of the bromophenol blue indicator are added into each flask, and neutralization with 0.2 M NaOH is carried out until greyish-blue colour appears. Weighted portions of the substance under investigation, 0.3–0.5 g, are added to thus prepared neutral oximating solutions. Weighting is carried out with the analytical

balance at the accuracy of 0.0001 g. After mixing, the mixtures are kept in flasks for 30 min. Then the released hydrochloric acid is titrated with 0.2 M NaOH solution until stable greyish-blue colour appears; colouring is compared with the colour of the reference solution. The reference solution: 20 mL of distilled water and 50 mL of the 0.5 M solution of hydroxylamine hydrochloride, six drops of the indicator, neutralized with the 0.2 M NaOH solution until greyish-blue colour appears (the blank experiment).

The content X of carbonyl groups in mixture is determined using equation

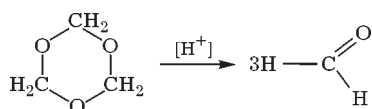
$$X = (a - b)0.0056 \cdot 100K/g$$

where a , b are the volumes of the 0.2 M NaOH solution spent for titration of the weighted portion of the mixture under investigation and for neutralisation of oximating solution, respectively, mL; 0.0056 is the amount of carbonyl groups corresponding to 1 mL of the 0.2 M NaOH solution, g; K is correction for the 0.2 M NaOH solution; g is the weighted portion of the substance to be analysed, g [16].

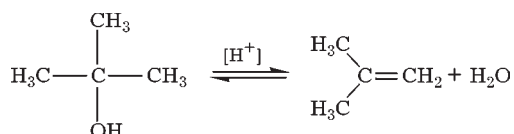
RESULTS AND DISCUSSION

On the basis of the analysis of possible versions of the synthesis of isoprene from 1,3,5-trioxane and trimethylcarbinol, and the composition of products, the following reaction mechanism was proposed:

1. Decyclization of trioxane in the acid medium to form formaldehyde:



2. Dehydration of trimethylcarbinol on the acid catalyst at a temperature about 120 °C to form isobutylene:



3. Interaction of isobutylene with formaldehyde according to Prins reaction in the presence of cation-exchange resin, with the formation of

Fig. 2. Dependence of isoprene yield on reaction time in the presence of the Granion D 001 catalyst ($T = 120^{\circ}\text{C}$, molar ratio trioxane/trimethylcarbinol = 1 : 15. Mass fraction of Granion D 001, %: 2.5 (1), 5.0 (2), 7.5 (3), 10 (4), 15 (5).

ballast water introduced into the reaction mixture and thus to decrease the amount of waste water substantially.

Thus, the new method developed by us allows us to obtain isoprene in one technological stage with lower energy consumption and reduced negative effect on the environment.

CONCLUSIONS

1. The possibility to single-stage synthesis of isoprene from 1,3,5-trioxane and trimethylcarbinol in the presence of the acid heterogeneous catalyst – cation-exchange resin – was established.

2. The composition of the reaction mixture was determined by means of gas-liquid chromatography.

3. Optimal conditions for the synthesis of isoprene were chosen.

4. The amount of waste water was reduced due to the use of 1,3,5-trioxane instead of the aqueous solution of formaldehyde, and cation-exchange resin as the heterogeneous catalyst.

5. Due to the conductance of isoprene synthesis in one technological stage under moderate conditions, energy consumption is decreased substantially in comparison with the two-stage method.

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