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CATALYSIS

Choice of a Catalyst and Technological Scheme for Synthesis of Solketal

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Abstract—Results are presented obtained in tests of various homogeneous and heterogeneous catalysts in a synthesis of solketal (2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane). It is shown that, all other conditions being the same, the highest catalytic activity is observed for sulfuric acid and beta zeolite. Data are presented on how the equilibrium constant of the reaction of glycerol ketalization depends on temperature. A technological scheme of the process for synthesis of solketal is suggested and its description is presented.

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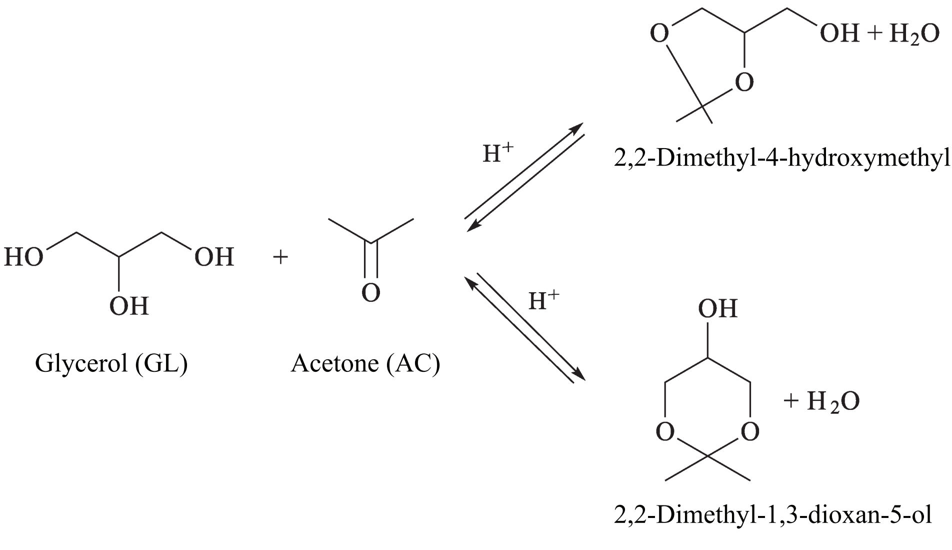
The interaction of glycerol wit acetone on acid-type catalysts yields two products: 2,2-dimethyl-4-hydroxymethyl-1,3-dioxolane, also named solketal, and 2,2-dimethyl-1,3-dioxan-5-ol. The amount of the latter in the reaction products commonly does not exceed 2–3%. The scheme of the occurring reactions is presented below:



(1)

In what follows, the term solketal will mean a mixture of these two isomers.

Solketal belongs to oxygenates, a group of lower alcohols and esters used as high-octane components of motor fuels. Use of oxygenates extends the service characteristics of fuels and, as a rule, improves their

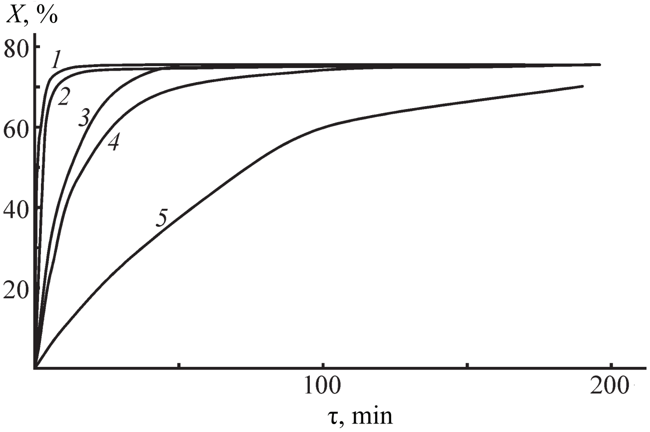


Fig. 1. Conversion X of glycerol in the ketalization reaction on various catalysts vs. time τ. (*1*) Sulfuric acid, (*2*) beta zeolite AO AZKiOS, (*3*) beta zeolite C814E, (*4*) Amberlist 35 dry ion-exchange resin, (*5*) KU-2-8 ion-exchange resin.

quality. Gasolines with oxygenates have improved detergent properties, combustion characteristics, and form a smaller amount of carbon monoxide and hydrocarbons in burning. In recent years, the increasing popularity has been gained by oxygenates produced from alternative raw materials and, in particular, from glycerol, a waste formed in production of a biodiesel fuel [1–3]. Solketal belongs to just this kind of products.

The present communication is devoted to choosing the most active and technologically convenient catalyst for synthesis of solketal and developing a technological scheme for obtaining this product.

EXPERIMENTAL

We used the following reagents: glycerol (special purity), acetone (chemically pure), rectified ethanol, and distilled water. As catalysts served sulfuric acid (chemically pure), Amberlist 35 dry (Dow), KU-2-8 cation-exchange resin preliminarily dried with acetone on a water bath, and beta zeolite CP814E (Zeolyst International).

The study was carried out in a glass reactor with reflux, cartridge for a thermocouple, and ground joint for introduction of a catalyst and sampling. The reaction mixture was agitated with a magnetic rabble. The temperature in the reactor was adjusted and measured with a set of devices including a TRM-101 single-channel microprocessor programmable temperature controller-meter and a solid-state relay, connected to the heating element of the magnetic rabble.

The reactor was charged with the following amounts of the reagents (g): glycerol 25.0, ethanol 19.0, and acetone 80.0. The acetone : glycerol molar ratio was 5 : 1. When being agitated, the reaction mixture was heated to a temperature of 40°C. The instant of time at which the catalyst was introduced into the reaction mixture was considered the reaction onset time. The reaction mixture was periodically sampled to analyze the reaction products.

The samples of the reaction mixture, taken for analysis, were neutralized with a 0.1 N NaOH solution at the instant of sampling. The reaction products were analyzed by gas-liquid chromatography on a Tsvet-800 chromatograph with a ZB-WAX capillary column and flame-ionization detector.

RESULTS AND DISCUSSION

All experiments on syntheses of solketal were performed by taking the amount of catalysts that provided the same and constant concentration of acid centers, equal to 2.3 mmol of H^+ per 124 g of the reaction mixture. The data on the concentration of acid centers in the heterogeneous catalysts were taken from their rating data. The results of these experiments are presented in the table.

The experiments demonstrated that, at the same number of acid centers in the reaction mixture, the highest rate of glycerol ketalization is provided by sulfuric acid. Reaching this result required the smallest amount of the catalyst: the content of sulfuric acid in the reaction mass was 0.095 wt %.

Beta zeolite (AO APCOS, Angarsk) was found to be the most active heterogeneous catalyst. At the same concentration of acid centers and amount of the catalyst in the reaction mass as those for beta zeolite CP814E (Zeolyst International), the initial rate of the reaction in which solketal is formed on Angarsk zeolite was nearly 3.5 times that on the beta zeolite CP814E. Amberlist 35 dry ion-exchange resin (Dow company) also demonstrated comparatively high initial rate and throughput, being only slightly inferior to Angarsk zeolite.

The data obtained suggest that the activity of the heterogeneous catalysts in the synthesis of solketal is determined by the nature of acid centers on the catalyst surface, by the fabrication conditions, and, presumably, by the composition and amount of impurities in the catalysts, rather than by the specific concentration of the acid centers.

Figure 1 shows how the conversion of glycerol into solketal depends on the experiment duration. The

Initial rates of solketal synthesis on various catalysts

Catalyst	Concentration of acid centers, mmol H^+/g_{cat}	Charged catalyst mass, g	Initial rate, M s^{-1}	Initial output capacity, M s^{-1} $g_{cat}{}^{-1}$
H_2SO_4	19.6	0.118	3.48×10^{-2}	0.295
Beta zeolite, AO APCOS, Angarsk	1.1	2.10	7.61×10^{-3}	3.6×10^{-3}
Beta zeolite CP814E, Zeolyst International	1.1	2.10	2.19×10^{-3}	1.0×10^{-3}
KU-2-8	4.6	0.50	3.00×10^{-4}	0.6×10^{-3}
Amberlist 35 dry	5.0	0.46	1.48×10^{-3}	3.2×10^{-3}

amounts of catalysts used in synthesis are listed in the table.

It follows from Fig. 1 that sulfuric acid and Angarsk beta zeolite make it possible to reach, already during the first 15–20 min, a 75–76% conversion of glycerol, which is the maximum and equilibrium conversion of glycerol in the reaction with acetone. This conversion is only observed in 50 min on beta zeolite CP814E and in nearly 110 min on Amberlist 35 dry ion-exchange resin.

Thus, the following two catalysts can be recommended for industrial manufacture on the basis of the experimental data: beta zeolite produced by AO Angara Plant of Catalysts and Organic Synthesis and sulfuric acid.

It is known that heterogeneous catalysts have, compared with homogeneous catalysts, a number of advantages, including the low expenditure of a catalyst per unit amount of the target product, absence of wastewater, no need to purify the reaction mass to remove the catalyst: zeolite is comparatively easily separated from the reaction mass and does not corrode the apparatus. This circumstance justified the development of a technological scheme for synthesis of solketal on the heterogeneous catalyst, beta zeolite.

A specific feature of the synthesis of solketal is the low mutual solubility of the starting reagents, acetone and glycerol. As a result, the starting mixture of the reagents is heterophase at a glycerol : acetone molar ratio of 5 : 1 and rapidly stratifies without a vigorous agitation. The reaction mass becomes homogeneous only when containing increased contents of solketal and water , which corresponds at a temperature of 40°C to a glycerol conversion $X \geq 40\%$.

The most efficient apparatus for a heterogeneous-catalytic synthesis of solketal is a column reactor packed with a fixed catalyst bed. The mixture of the starting reagents is delivered into the upper part of the reactor, with the catalyst bed uniformly sprayed. The reaction of glycerol with acetone occurs in a film flowing down over the surface of catalyst particles. However, the starting emulsion stratifies in the upper part of the reactor, in which the conversion of glycerol is still lower than 40%, and a glycerol film hindering the approach of acetone to the active surface of the catalyst is formed on its surface [4].

For an apparatus with fixed catalyst bed to operate with high efficiency, it is necessary to provide the maximum possible wetting of its surface, which is commonly reached at spraying densities of 3–5 m^3 m^{-2} h^{-1}. However, experiments demonstrated that, even at a spraying density of 0.15 m^3 m^{-2} h^{-1}, the glycerol film on the catalyst surface becomes so thick and flows down so slowly that this leads to flooding of the catalyst and to accumulation of an emulsion of starting reagents over its bed. Thus, it is nearly impossible to perform the process without a preliminary homogenization of the mixture of the starting reagents.

This problem is, as a rule, solved by introduction into a binary mixture of a third component raising the mutual solubility of glycerol and acetone. In synthesis of solketal, the role of this additive is played by ethanol, which homogenizes the mixture of the starting reagents, yields no by-products, and can be easily evaporated from the reaction mixture and be recycled into the synthesis stage. It was found experimentally that the glycerol : ethanol ratio should not be less than 1 : 1.

However, using ethanol as a homogenizing reagent will complicate the technological scheme of the process due to the installment of a mixing apparatus at the inlet

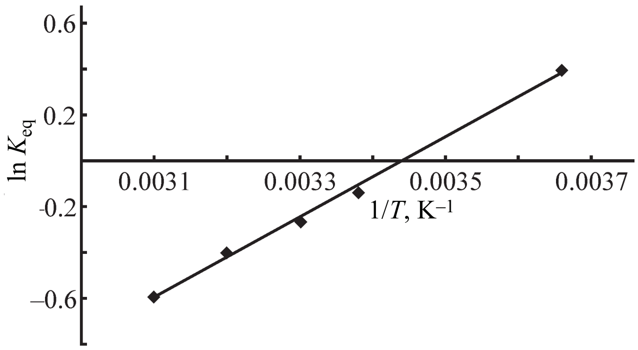


Fig. 2. Dependence of the equilibrium constant K_{eq} of the reaction of solketal synthesis on temperature T.

of the reactor for synthesis of solketal. In addition, the introduction of a third component into the system will cause a lower rate of the solketal formation reaction due to the decrease in the concentration of the starting reagents and will require an additional energy expenditure in the stage in which ethanol is separated from the target product.

It is known that the reaction of glycerol ketalization is of equilibrium type, which results in that the conversion of glycerol in industrial technologies does not exceed 75–80%. To improve the economic efficiency and solve ecological problems, the technological scheme should include the stage in which the unreacted glycerol is isolated to be recycled into the synthesis stage. Because glycerol is the highest boiling product, it will be collected in the still product of the third rectification column in the stage of separation of the reaction mass. Consequently, this glycerol will contain all tarry products formed in the stills of al the three columns and also the technological "garbage," including the products of equipment corrosion, parts of liners, and machinery oil that can penetrate into the system from stirrers, pumps, etc.

The recycling of this glycerol into the synthesis reactor packed with a heterogeneous catalyst will lead to a gradual deactivation of the catalyst due to the adsorption of above impurities on its surface.

Experiments demonstrate that, even in operation without glycerol recycling, the activity of heterogeneous catalysts decreases in the course of time [5–7]. The rate of this process directly depends on the quality of glycerol. If raw glycerol containing mineral salts, soaps, and fatty acids is used, the deactivation of the catalyst is very fast [5]. However, these processes are inevitable even in the case of a distilled glycerol [6, 7]. The reason is that, in all probability, even distilled glycerol contains trace amounts of mineral salts, fatty acids, and glycerol esters [8, 9]. In addition, side reactions of the aldol condensation of acetone may occur on acid centers of the catalysts, which also poisons the catalyst [10].

Thus, the recycled glycerol and products of side reactions comparatively rapidly deactivate a catalyst and causes its replacement. Because the cost of beta zeolite is several thousand roubles per kilogram, the need to regularly replace the catalyst adversely affects the economic attractiveness of this technology for synthesis of solketal.

In contrast to that described above, the technology for solketal synthesis with the use of a homogeneous catalysis does not require an additional component for homogenization of the system. The starting reagents (glycerol, acetone, and sulfuric acid) are continuously delivered into the mixing reactor. The residence of the reaction mixture in the mixing apparatus for more than 10–15 min (at a sulfuric acid concentration of 0.1 wt %) is sufficient for reaching the 40–50% conversion, which guarantees that a homogeneous mixture of reaction products is formed. Because the reaction mixture is homogeneous and contains a catalyst, the reaction can further occur even without agitation until the equilibrium is attained.

One of possible variants is to accumulate and store reaction products in vessels. This is quite a reasonable solution because industrial plants nearly always have a gap between vessels used in different stages of the process.

It should be noted that the equilibrium constant of the reaction in which glycerol interacts with acetone grows with decreasing temperature. Figure 2 shows the experimentally obtained temperature dependence of the equilibrium constant of the reaction of glycerol ketalization. The dependence is described by the equation

$$\ln K_{eq} = 1745.8\frac{1}{T} - 6.0. \tag{2}$$

Using the Van't Hoff's isobar equation, we calculated from the data in Fig. 2 the heat effect of the reaction to be $\Delta H = -14.5$ kJ mol^{-1}.

The reaction is exothermic. When solketal is synthesized in a 5-fold molar excess of acetone relative to glycerol, the released heat is sufficient for heating the reaction mixture by at most 12° (with the loss of heat disregarded).

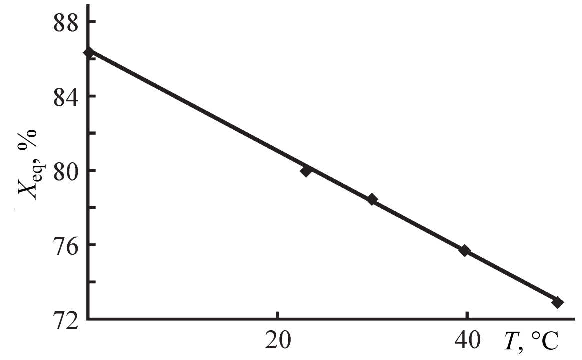


Fig. 3. Dependence of the equilibrium conversion X_{eq} of glycerol on temperature T. Glycerol : acetone molar ratio = 1 : 5, starting glycerol of D-98 brand.

Because the equilibrium conversion of glycerol grows as temperature is lowered (Fig. 3), it is reasonable to cool the vessels used to keep the reaction products.

The reaction products are separated in a set of rectification columns. The excess acetone is evaporated in the first rectification column and recycled into the synthesis stage. Water is evaporated in the second rectification column, and the commercial product, solketal, in the third column in a vacuum.

Because the reaction in which solketal is synthesized is of the equilibrium type, the content of water in the circulated acetone evaporated in the first rectification column should not exceed 1.3 wt %. With consideration for the fact that the process is performed at a 5-fold molar excess of acetone and a large reflux ratio of 4 is required in its rectification, more than 80% of the energy expenditure by the system for separation of the reaction products is accounted for by the column for evaporation of acetone.

Prior to being separated into reaction products, the reaction mixture containing a catalyst, sulfuric acid, is neutralized.

Figure 4 shows the flow diagram of the process in which solketal is synthesized.

Previously, the results of a study of an alternative way to recover solketal from reaction products by the extraction method have been reported [12]. It was shown that, if acetone is evaporated from reaction products, solketal can be extracted from the remaining mixture of components with benzine containing 30–35 wt % aromatic compounds. In this case, the content of solketal in the resulting benzine will be no less than 4.5 wt %. Despite that this method of obtaining benzine enriched with solketal is attractive, there are several reasons why its implementation is impractical. First, the whole amount of acetone is to be evaporated prior to the extraction of solketal. Because the rectification of acetone consumes most part of energy, the recovery of solketal from

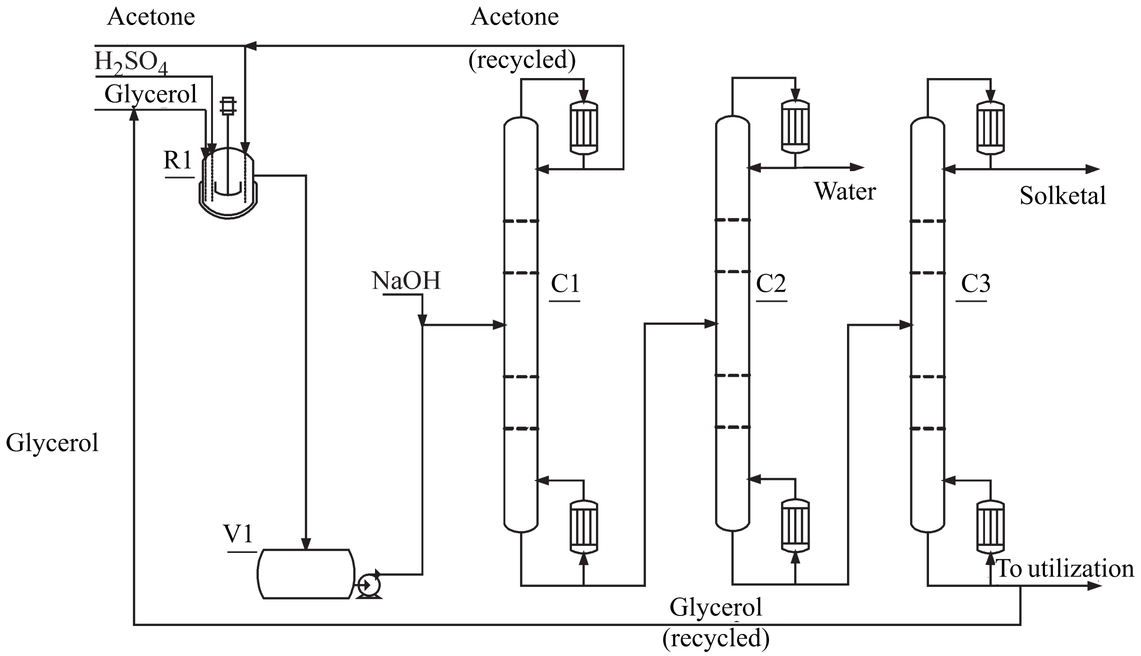


Fig. 4. Flow diagram for manufacture of solketal. R1 designates the reactor; V1, vessel; C1–C3, rectification columns.

reaction products by the extraction method and that by the rectification on three columns are approximately the same in energy expenditure.

Second, the recovery of solketal by the extraction method requires large flows of benzine in the technological scheme and, accordingly, a rather large number of vessels for the starting benzine and that enriched with solketal. And this entails not only a gross expenditure of energy and materials, but also a high fire hazard of the installation. In view of these data, the technological scheme for recovery of solketal by the extraction method is not considered an industrially usable technology.

CONCLUSIONS

The experiments performed in the study demonstrated that two catalysts can be used for industrial production of solketal: beta zeolite manufactured y AO Angarsk Plant of Catalysts and Organic Synthesis and sulfuric acid. The technological scheme based on the application of a heterogeneous catalyst has a number of disadvantages, the main of which are the following: need to introduce and additional component (ethanol) for homogenizing the reaction mixture and, accordingly, to install and additional reactor with a stirrer for dissolution of the starting reagent; gradual deactivation of the catalyst; impossibility of recycling the unreacted glycerol; and high cost of the catalyst. The technological scheme with sulfuric acid is devoid of these shortcoming, is very simple and reliable, and can provide a nearly 100% yield of solketal due to the recycling of glycerol.

The synthesis of solketal in the presence of sulfuric acid is the most reasonable and economically efficient technology for production of this compound. A flow diagram for synthesis of solketal was suggested and its description was given.

REFERENCES

1. Maksimov, A.L., Nekhaev, A.I. , and Ramazanov, D.N., *Petroleum Chem*., 2015, vol. 55, no. 1, pp. 3–24.
2. Maksimov, A.L., Nekhaev, A.I., Ramazanov, D.N., et al., *Petroleum Chem*., 2011, vol. 51, no. 1, pp. 61–69.
3. Varfolomeev, S.D., Volieva, V.B., Usachev, S.V., et al., *Catal. Ind*., 2011, vol. 3, no. 1, pp. 11–14.
4. Dmitriev, G.S., Terekhov, A.V., Khadzhiev, S.N., et al., *Russ. J. Appl. Chem*., 2016, vol. 89, no. 1, pp. 45–50.
5. Gemma, V., Melero, J.A., Morales, G., et al., *Green Chem*., 2010, no. 12, pp. 899–907.
6. Oliveira, P.A., Souza, R.O.M.A., and Mota, C.J.A.*, J. Braz. Chem. Soc*., 2016, vol. 27, no. 10, pp. 1832–1837.
7. Stawicka, K., Diaz-Alvarez, A.E., Calvino-Casilda, V., et al.*, J. Phys. Chem*., 2016, vol. 120, pp. 16699–16711.
8. GOST (State Standard) 6824–96, *Distilled Glycerol, General Technical Specifications.*
9. GOST 6259–75, *Reagents, Glycerol, Technical specifications.*
10. Clarkson, J.S., Walker, A.J., and Wood, M.A., *Org. Process Res. Dev*., 2011, no. 5, pp. 630–635.
11. Zaharia, E., Bildea, C.S., and Muntean, O., *U.P.B. Sci. Bull., Ser. B*, 2015, vol. 77, no. 2, pp. 1454–2331.
12. Terekhov, A.V., Dmitriev, G.S., Khadzhiev, S.N., et al., *Russ. J. Appl. Chem*., 2016, vol. 89, no. 4, pp. 639–643.