ISSN 0965-5441, Petroleum Chemistry, 2011, Vol. 51, No. 1, pp. 61–69. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © A.L. Maksimov, A.I. Nekhaev, D.N. Ramazanov, Yu.A. Arinicheva, A.A. Dzyubenko, S.N. Khadzhiev, 2011, published in Neftekhimiya, 2011, Vol. 51, No. 1, pp. 62–69.

Preparation of High-Octane Oxygenate Fuel Components from Plant-Derived Polyols

A. L. Maksimov, A. I. Nekhaev, D. N. Ramazanov, Yu. A. Arinicheva,
A. A. Dzyubenko, and S. N. Khadzhiev
Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia
e-mail: max@ips.ac.ru

Received August 27, 2010

Abstract—The ketalization of polyols (glycerol, xylitol, xylose) in the presence of a number of heterogeneous acid catalysts has been studied. It has been shown that zeolite catalysts exhibit high activity in the formation of the acetone ketal of glucose in a flow system with the quantitative selectivity for the 1,2-product. The best catalyst is zeolite beta; in the presence of this zeolite and excess acetone, the yield is over 90% or, in the case of the structured reactor, even greater than 98% It has been shown that zeolite-based systems catalyze the formation of ketals of xylitol and xylose with a yield of up to 50% in the presence of excess acetone.

DOI: 10.1134/S0965544111010117

The manufacturing of motor fuel components with improved environmental characteristics from biomass is a possible way to broaden the resource base of the contemporary fuel industry. The use of oxygen-containing fuel components (ethanol, biodiesel) produced from biomass has become widespread in several countries [1–3] and stimulates the search for new oxygenate components of motor fuels. It should be noted that the production of both ethanol and methyl esters of fatty acids is accompanied by the formation of by-product polyols, namely, pentose from hemicellulose in the case of alcohol and glycerin in the case of biodiesel [4]. For example, 100 kg of glycerol per ton of biodiesel is produced, and its total output at the present level of production of this form of fuel is more than 1 million tons.

Polyols cannot be used as a component of traditional hydrocarbon fuels because of the presence of several polar hydroxyl groups in their molecular structure and, hence, a low solubility in hydrocarbons. Modification of polyols, in particular, via acylation of their hydroxy groups [5, 6] leads to an increase in hydrophobicity and allows the use of the resulting derivatives as fuel additives [7–9].

One way of modifying polyols is the synthesis of ketals, the derivatives produced in the reaction with ketones. It was shown that the products of ketalization of polyols with acetone can serve as a high-octane component of gasolines and reduce their tendency toward gumming, lower the freezing point of diesel fuels, and improve their lubricating properties [10, 11]. Thus, the acetone ketal of glycerol (solketal) has a blending octane number of 98 [12]. Its admixture in an amount of 1–5% significantly enhances the oxidation stability of gasoline [13]. In a mixture with ethanol, it can dramatically increase the octane number of gasoline: a 10% ethanol additive increases the RON of AI-80 gasoline by 1.7, whereas the additional introduction of 10% solketal increases it by 9.4 units. Note that the breaking point for the fuel obtained is below –30°C. When the ketal of arabinose is used as an additive for AI-80 gasoline with 10% ethanol, the motor octane number of the resulting fuel is greater than 95 [14].

The formation of ketal via the reaction of a polyol with acetone involves the formation of water and usually requires a combination of acid catalysis with a dehydrating agent. Acetone itself can act as an agent of this kind [15, 16]. Both homogeneous (sulfuric acid, toluenesulfonic acid) and heterogeneous catalysts can be used for glycerol ketalization with acetone. Of the latter catalysts, cation-exchange resins (Amberlyst DPT-1, Amberlyst-15 [17], Amberlyst-36 [18]), montmorillonite K-10 [19], zeolites [17, 20], silica-supported heteropoly acids [21], and mesoporous silicates bearing arylsulfonate groups [22] are worth mentioning. The best results (90% yield of solketal with high selectivity) were achieved with a sixfold excess of acetone in a batch reactor with the evaporation of acetone in the second stage of the process [22] or with the use of a membrane reactor for water removal [19].

The ketalization of saccharides with acetone over heterogeneous catalysts has been intensively studied with various types of catalysts: organic and inorganic acids, such as toluenesulfonic and tetrafluoroboric acids [23, 24]; Lewis acids (iron(III) chloride [25], aluminum chloride [26], vanadyl trifluoroacetate [27]); and other heterogeneous systems [28–32]. However, the catalyst could not be reused in most cases, and the yields were low.

Table 1. Characterization of the catalysts used in the study

Catalyst	Acidity, mequiv H^+/g*	Surface area, m^2/g	Pore volume, cm^3/g	Pore diameter, nm	Si/Al of active component
KU-2 in the H form	1.4	15	2.7	–	–
Zeolite beta Zeolyst CP811Tl	0.81	752	0.58	0.69	20
Zeolite beta Zeolyst CP814E	1.4	680	0.62	0.70	12.5
Zeolite Y	2.1	629	0.56	0.74	2.5
Tseokar-600**	0.54	321	0.5	–	5
Zeolyst ZD 04028***	0.97	492	0.58	0.78	10
F4SF****	0.96	0.06	–	–	–
SiO_2/25%-F4SF	0.24	231	0.13	0.73	–

Notes: * According to the manufacturers' data for the zeolite catalysts.

** Zeolite Y, 10%; lanthanide as the oxide, 1.8%; and Na_2O, no more than 0.55%.

*** 85% mordenite in the H form; Na_2O, no more than 0.06%.

**** A copolymer of tetrafluoroethylene and perfluoro-3,6 dihydroxy-4-methyl-7-octene-sulfonic acid.

In this work, we studied the ketalization of glycerol in a flow system and that of monosaccharides (xylose, xylitol) in a batch reactor using a number of catalysts based on solid acids.

EXPERIMENTAL

The catalysts used in this study were the KU-2 cation-exchange resin in the acid form, fluorinated sulfonated cation exchanger F-4SF (tetrafluoroethylene copolymer with perfluoro-3,6-dihydroxy-4-methyl-7-octenesulfonic acid) in the acid form with an equivalent weight of 890, the silica gel-supported polymer F-4SF (25%), zeolite beta Zeolyst CP811TL in the acid form, zeolite beta Zeolyst CP814E in the acid form, zeolite Y (Aldrich) in the acid form, the catalyst Tseokar 600 based on zeolite Y (10% zeolite Y), and mordenite-based catalyst Zeolyst ZD 04028. The acid forms of zeolite Y (Aldrich) and zeolite beta (Zeolyst CP814E) were obtained by calcining the NH_4 forms of commercial samples at 550°C over 6 h in a dry air stream.

The catalyst based on the supported polymer F-4SF was prepared as follows. To a calculated volume of a sulfonated perfluoropolymer solution (containing 7.2% F-4SF with an equivalent weight of 890) in isopropanol, 93 ml of 0.4 mol/l NaOH solution and then 75 ml of water were poured with vigorous stirring. A mixture of 138 g of tetraethyl orthosilicate with 20 ml of water and several drops of HCl was added to the resulting solution, evaporated in vacuum to have a volume of 330 ml. The gel produced was held in air at room temperature for 8 h and then dried to the air-dry state at 95°C over 2 days. The resulting composite was treated with 300 ml of 15% nitric acid at 70°C for 7 h. The solid phase was filtered off, washed with distilled water, and dried over 24 h in a vacuum at 100°C to give a glassy solid of 59 g mass (yield 95%).

The amount of acid sites in the F-4SF-based catalyst and the KU-2 cation exchanger was determined by acid–base titration. A weighed sample was vigorously stirred in a 10% NaCl aqueous solution over 4 h, then the solid phase was filtered off and the solution was titrated with 0.01000 mol/l NaOH (with phenolphthalein as the indicator). Data on the total acidity of zeolites were provided by suppliers and further confirmed by means of this method.

The characteristics of the porous structure of the given zeolite samples and the supported F-4SF catalyst were determined with an ASAP-2010N analyzer (Micrometrics). Prior to analysis, a sample was evacuated at 200°C for 6 h to a pressure of 1×10^{-3} atm. The nitrogen adsorption–desorption isotherm was recorded at 77 K. The porous-structure characteristics were calculated using the ASAP-2010N dedicated software. The samples were characterized by the BET specific surface area, the pore volume (at $p/p_0 = 0.95$), and the pore diameter. The pore size distribution curve was obtained using the BJH method. The characteristics of the catalysts are listed in Table 1. The reagents used were glycerol and acetone of analytical grade, xylose (Aldrich), and xylitol (Fluka) without preliminary treatment.

Glycerol ketalization with acetone in a flow system was performed using a setup that included two Gilson 305 pumps, a standard Gilson mixer in which the streams were mixed, and a reactor of 15 ml in volume. The reaction temperature was monitored with a thermocouple placed inside the reactor. The average yield for 4 h of the reaction was determined. The catalyst particle size was 15 times smaller than the diameter of the reactor to minimize jet breakthrough. The zeolite and F-4SF/SiO_2 catalyst samples were tableted (compaction pressure of 3 t/cm^2), the tablets were ground, and a 1–1.5 mm fraction of particles was taken. For the Tseokar-600 and Zeolyst ZD 04028 catalysts, such a fraction for experiments was collected after grinding the catalysts as purchased. A few experimental runs were performed in the "structured reactor" designed for this purpose [33].

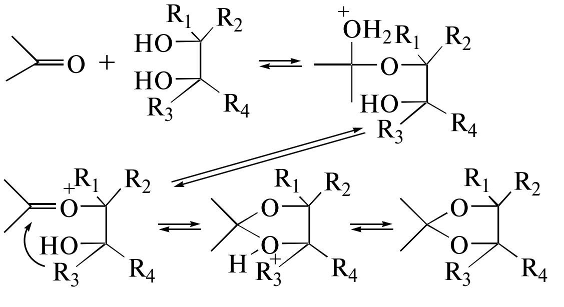
The ketalization reaction of xylose and xylitol was investigated in a thermostated glass reactor equipped with a reflux condenser. In some experiments, a cartridge packed with molecular sieves 4A preliminarily dried in a vacuum was installed between the condenser and the reactor.

The glycerol, xylose, and xylitol ketalization products were analyzed on a Kristallyuks 4000 M chromatograph equipped with a flame ionization detector. The column dimensions were 30 m × 0.4 mm, and the stationary phase was SB-5-Octyl (Supelco). The temperature was programmed from 60 to 220°C. A calibration mixture with an exactly known ketal concentration was used for quantitative analysis.

The progress of the reactions involving monosaccharides and the product composition were also monitored using NMR spectroscopy. After the reaction, acetone was distilled off in a vacuum, and the resulting sample was dissolved in deuterated DMSO. Its spectra were taken with an Advance Bruker instrument operating at a frequency of 400.13 MHz. The chemical shifts are given on the δ scale (ppm) relative to TMS (0.00 ppm). The standard was DSS (3-(trimethylsilyl)propanesulfonic acid, δ 0.015 ppm). In the case of GLC analysis, the ketals of xylose and xylitol were determined directly in the reaction mixture with the use of an internal standard (toluene).

RESULTS AND DISCUSSION

The formation of ketals of polyols is an acid-catalyzed reaction, which proceeds according to the mechanism shown below:



The reaction suggests the protonation of the ketone oxygen and requires the use of acid catalysts that have a sufficient strength to mediate such protonation and the formation of the oxocarbonium ion [34]. At the same time, it is known that catalysts with very strong acid sites are unnecessary for the formation of acetals and ketals; it is sufficient to have a combination of medium and weak acid sites [35]. Therefore, as a glycerol ketalization catalyst, systems containing zeolites with different pore sizes, such as zeolite beta (6.6 × 6.7 nm pores), mordenite (6.5 × 7 nm pores), and zeolite HY (7.4 × 7.4 nm pores), were selected, as well as systems based on the F-4SF polymer (Russian analogue of Nafion). The activity of the catalysts was compared with that of the KU-2 sulfonated cation exchanger in the H form, which is one of the most common catalysts for this reaction studied under the batch reactor conditions.

Table 2. Ketalization of glycerol at different acetone/glycerol ratios

Catalyst	Acetone/glycerol, mol/mol	
	2	6
KU-2 (60°C)	55	85
Tseokar-600 (40°C)	32	64
Zeolite beta Zeolyst CP811Tl (35°C)	62	85
Zeolite beta Zeolyst CP814E (35°C)	60	82
Zeolite HY	21	37

The results are shown in Table 2 and Figs. 1–6. Note that the condensation of polyols generally leads to the formation of five-membered cycles, whereas the formation of six-membered rings is less favorable owing to the fact that one of the methyl groups in the final product is in the axial position of the chair conformation [36]. In all cases, the selectivity of the most thermodynamically stable product 1,2-diketal was quantitative in the presence of acid catalysts. Moreover, the conversion of acetone into its condensation products did not exceed 1% in all runs. As can be seen, the activity of the zeolite-based catalysts is somewhat lower than that of KU-2 at an acetone/glycerol ratio of 2 (Figs. 1–3). The catalysts based on zeolite beta are the best. The yield of ketal on these catalysts reached 62% at 35°C, whereas the maximum yield over KU-2 was 68% at 70°C. The lowest activity was observed for the system containing bare zeolite HY (Fig. 4). A comparison of the yields of ketal per acid site shows that the catalysts based on zeolites beta exhibit the maximum specific activity (Fig. 5). Of these, the catalyst with the largest silica ratio and the highest hydrophobicity (zeolite beta Zeolyst CP811Tl) turned out to have the highest activity.

Note that the rate-determining step in the formation of cyclic ketals from polyols is the oxocarbonium

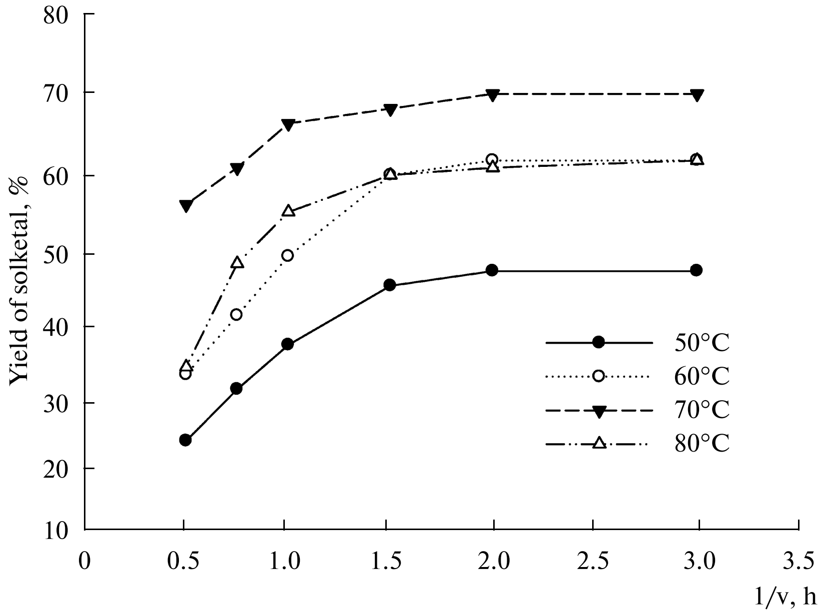


Fig. 1. Ketalization of glycerol over KU-2. Acetone/glycerol = 2 (mol/mol).

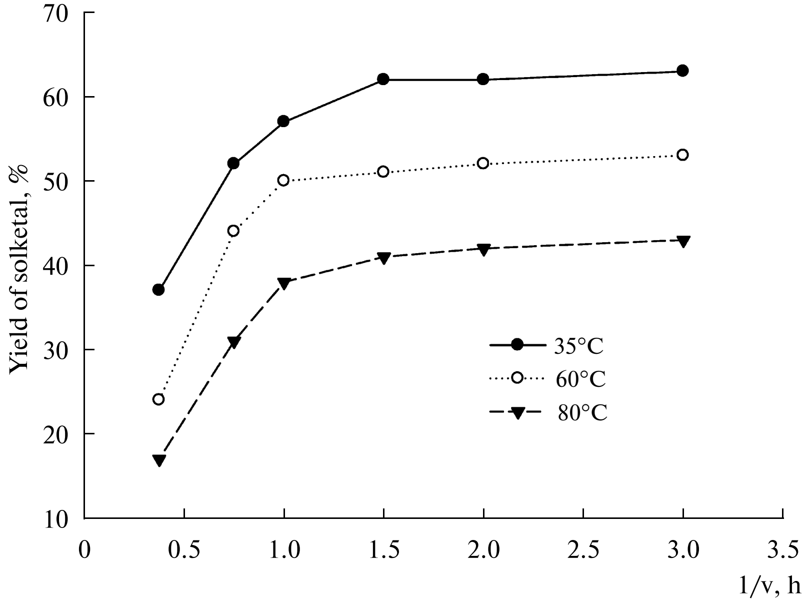


Fig. 2. Ketalization of glycerol over zeolite beta Zeolyst CP811T1.

ion transformation caused by the nucleophilic attack of the hydroxyl group on the carbon of the oxo group [34]. This step does not require the specific acid catalysis, thereby determining the absence of explicit dependence of the reaction rate on the strength and number of acid sites. It is likely that the magnitude of the reaction rate is associated with stabilization of the transition state, which is similar to the oxonium ion in nature, due to the interaction with the catalyst, in particular, in the zeolite cavity. The pore size of the catalyst and adsorption properties of the surface are also of substantial importance then [37, 38]. If a bulky intermediate does not fit to the zeolite cavity or is too loose in it and if the surface hydrophilicity is too high, the

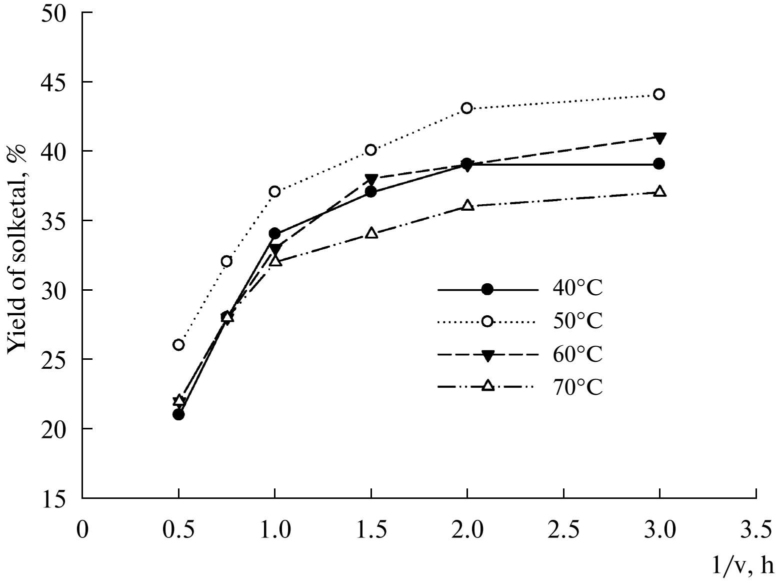


Fig. 3. Ketalization of glycerol over zeolite catalyst Tseokar-600. Acetone/glycerol = 2 (mol/mol).

reaction rate is significantly lower. This may be one of the reasons behind the low activity of the unmodified zeolite HY. The systems based on zeolite MFI with a small pore size showed a significantly lower activity even in the batch reactor. A similar effect was observed earlier in the case of formation of the acetylnaphthalene ketal of 1,2-propanediol over zeolite catalysts [39]. The importance of the matching of the size and shape of the adsorbate (polyol) molecule to zeolite pores for effective adsorption has been shown in [40] using zeolites beta, Y, MFI, and mordenite as examples.

Since all the processes involved in the formation of ketals are reversible, an excess of acetone relative to glycerol in the system is of particular importance for attaining a high yield (Table 2). A similar effect of excess acetone was revealed earlier during the ketalization over acidic cation exchangers, sulfonated mesoporous silica gel, and supported heteropoly acids as catalysts in batch reactors [19, 21, 22].

The data presented in Table 2 show that a twofold increase in the acetone/glycerol ratio for these catalysts leads to a more than doubled rise in the solketal yield for all catalysts, with the highest yield being achieved in the case of zeolites beta.

The change in the maximum attainable yield of solketal depending on the catalyst can be explained as follows. The concentration of adsorbed water is high for more hydrophilic catalysts, which displaces the equilibrium towards the reactants and reduces the yield of the ketal. For hydrophobic catalysts, the adsorption of glycerol is, in contrast, too low. The maximum activity is achieved at an optimal ratio of the surface concentrations of acetone and glycerol.

The adsorption of acetone on zeolites is largely due to the polarity of their surface, which is significantly lower for zeolite beta than for mordenite or zeolite Y, even with comparable silica ratios [40, 41]. In addition, the higher hydrophilicity of the surface of zeolite Y leads to retention of water in the pores, thus reducing its activity in esterification reactions at low temperatures [42]. Apparently, as a result of this retention, the maximum activity is achieved for zeolite beta with a Si/Al ratio of 20, while the zeolite with Si/Al = 12.5 is less active. An even lower activity is observed for the mordenite-based catalyst.

A relatively high specific activity of the catalyst Tseokar-600 containing as low an amount of zeolite Y as 10% can be explained by both the presence of rare-earth ions in its composition elements and the catalytic activity of the matrix, the amorphous aluminosilicate. It is possible that the ketone oxygen interacts with them as with Lewis acids, thereby promoting the adsorption of the ketone and increasing the reaction rate [43].

The temperature dependence of the solketal yield on the catalysts used can also be explained by changes in the adsorption equilibrium for the reactants (Figs. 4, 5). The zeolite catalysts showed the maximum activity at low temperatures when the saturated vapor pressure of acetone is low. The yield was 40–62%, significantly higher than that on the polymer-based catalysts at this temperature. A rise in the temperature leads to a decrease in the amount of volatile acetone in zeolite pores, and the activity of zeolite-containing catalysts decreases with an approach to 70°C. For polymers, the adsorption process of acetone and glycerol is associated with swelling and leads to a rise in the rate up to 70°C [44]. In the case of the sup-

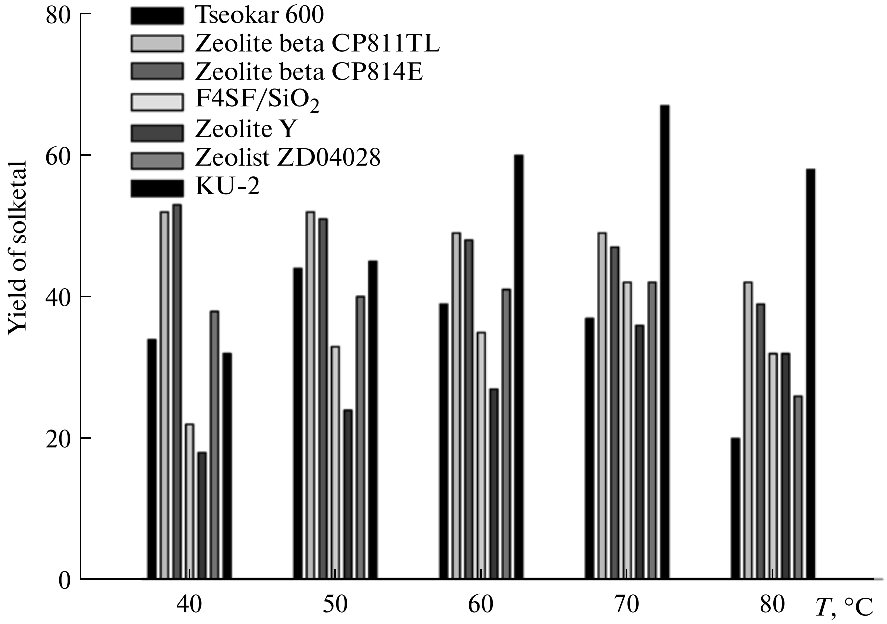
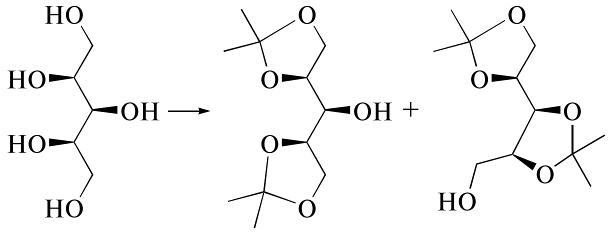


Fig. 4. Yields of solketal at different temperatures. Space velocity, 0.6 h^{-1}, acetone/glycerol = 2 (mol/mol).

ported catalyst based on the fluorinated polymer F-4SF, the low polarity of the fluorinated chains may determine the low adsorption of glycerol and does not allow for a high yield of ketal. At temperatures above 70°C, the yield of ketal was significantly reduced on all the catalysts, a fact that is apparently due to a sharp drop in the acetone content in the liquid phase with the increasing temperature. According to published data [16], the amount of acetone in the liquid phase is at most 12% even at 75°C, versus more than 65% at 70°C for the initial acetone/glycerol ratio of 2.

Based on these results, we found it appropriate to run the reaction in the “reactor with a structured regime” [33] designed by S.N. Khadzhiev and I.M. Gerzeliev for processes that require a substantial excess of one component (Fig. 6). In this case, the ketal yield over the catalyst based on zeolite beta increased from 52 to 80% at 65°C and from 85 to 98% at 35°C. High conversion and selectivity remained up to space velocities of 10 h^{-1}.

To investigate the ketalization of sugars under acid catalysis conditions, we selected two pentoses that differ in their structure but have the same number of carbon atoms in their molecules: xylose (monosaccharide capable of forming the pyranose and furanose forms) and xylitol (pentahydric alcohol with the linear structure of the hydrocarbon chain). The formation of the corresponding ketals of xylitol can be represented by the following scheme:



According to the NMR and GC–MS data, the two possible ketals are produced in roughly equal proportions. The overall yield of ketals approaches 50% for 48 h on all of the catalysts examined at an acetone/xylitol ratio of six in the reaction conducted in refluxing acetone. Note that in order to achieve the maximum yield, it is necessary to periodically distill acetone off after the end of the reaction or to use a drying agent to remove water from boiling acetone. In the latter case, high product yields are achieved within 5 h of the reaction. It is noteworthy that the zeolite beta Zeolyst CP811Tl exhibits even a somewhat higher activity as compared to the cation exchangers. The zeolite Zeolyst CP814E with a smaller Si/Al ratio shows a substantially lower activity, apparently due to less optimal surface concentrations of the reactants (Table 3).

We have previously shown that in the presence of a large excess of acetone (above 10 mol), xylose is ketalized over different catalysts based on solid acids. In this work, we investigated ketalization at a sixfold molar excess of acetone. The main product is ketal with the furanose structure according to NMR data, and its selectivity is close to 100%:

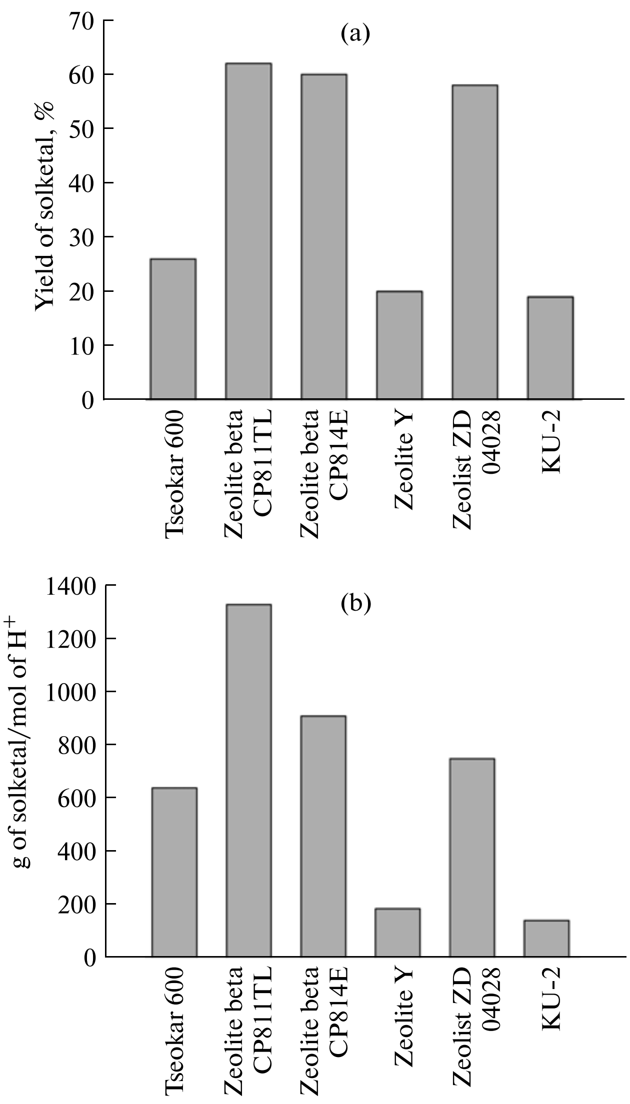
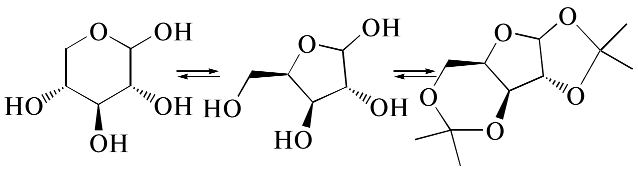


Fig. 5. Yields of solketal and the specific activity of catalysts in the solketal synthesis at 35°C. Space velocity, 0.6 h^{-1}, acetone/glycerol = 2 (mol/mol).



The reaction follows several stages involving the formation of the energetically unfavorable furanose form of xylose, which significantly slows down the process because of a very low solubility of the substrate in acetone and requires the reaction time to be extended to 48 h. In addition, diffusional constraints have a significant effect on the reactions of sugars over solid acid catalysts [45, 46]. The yield on the KU-2 cation-exchange resin and the supported F-4SF polymer at an acetone/xylose molar ratio of three was 20% even after 2 h, whereas that on other catalysts did not exceed a few percent. The yield on the zeolites beta was low and did not exceed 34% within 48 h, even in experiments involving the removal of water by distilling off acetone. The yield on zeolite Y was about 55%.

Table 3. The yield of xylitol ketalization products at 55°C, 6 h

Catalyst	Acetone/xylitol ratio (mol/mol)	Yield of ketals, %
KU-2 in the H form	6	48
SiO_2/25% F4SF	6	47
F4SF	6	19
F4SF	12	41
Zeolite beta Zeolyst CP811Tl	6	48
Zeolite beta Zeolyst CP811Tl	12	53
Zeolite beta Zeolyst CP814E	6	12

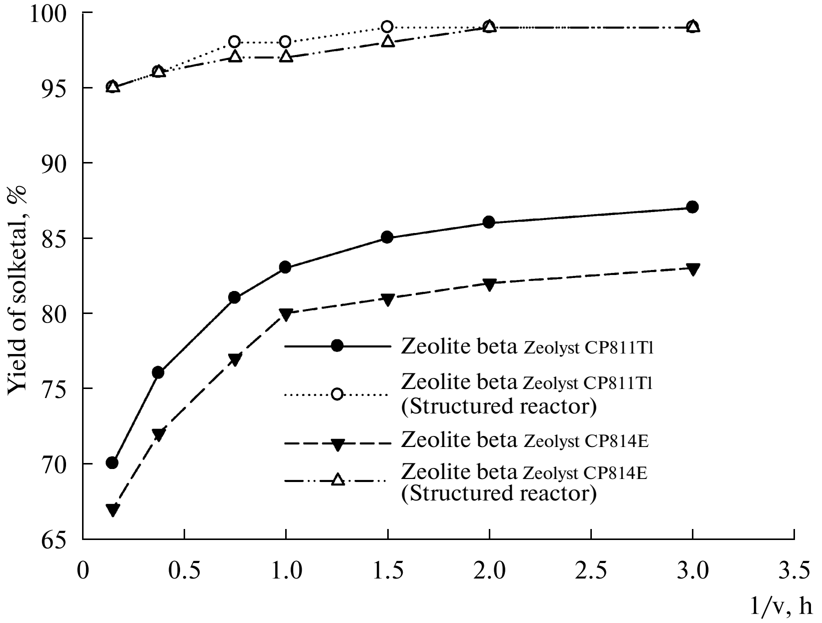


Fig. 6. Ketalization of glycerol on zeolites. Acetone/glycerol = 6 (mol/mol), 35°C.

Apparently, as in the case of other zeolite-catalyzed transformations of sugars [47], the higher yield in the latter case was due to the larger size of zeolite pores and, to a lesser degree, to the adsorption properties of the surface.

ACKNOWLEDGMENTS

This work was supported by the Russian Academy of Sciences under Presidium program no. 19 and the president of the Russian Federation under the program for supporting young Russian doctors of science, grant no. MD 793.2009.3.

REFERENCES

1. S. Yeh, P. Nicholas, N. P. Lutsey, and N. C. Parker, Environ. Sci. Technol. **43**, 6907 (2009).
2. *Country Analysis Briefs: Brazil* (Energy Information Administration, U.S. Department of Energy, Washington, DC, 2009).
3. Directive 2009/28/EC of the European Parlament and of the Council, Off. J. Eur. Union. *L 140/16* (2009).
4. B. Kamm, P. R. Gruber, and M. Kamm, *Biorefineries—Industrial Processes and Products: Status Quo and Future Directions* (Wiley-VCH, 2006), vols. 1, 2.
5. M. C. Vale, G. S. Lopes, and S. T. Gouveia, Fuel **88**, 1955 (2009).
6. E. Garcia, M. Laca, E. Perez, et al., Energy Fuels **22**, 4274 (2008).
7. US Patent no. 5308365 (1994).
8. US Patent no. 5476971 (1995).
9. C.-H. Zhou, J. N. Beltramin, Y.-X. Fan, and G. Q. Lu, Chem. Soc. Rev. **37**, 527 (2008).
10. WO Patent no. 093015 (2005).
11. US Patent no. 0025417 (2004).
12. R. Wessendorf, Erdoel, Kohle, Erdgas, Petrochem. **48**, 138 (1995).
13. C. J. A. Mota, C. X. A. Silva, and N. Rosenbach, Energy Fuels **24**, 2733 (2010).
14. RU Patent no. 2365617 (2009).
15. US Patent no. 5917059 (1999).
16. J. S. Clarkson, A. J. Walker, and M. A. Wood, Org. Proc. Res. Dev. **5**, 630 (2001).
17. C. X. A. Silva, V. L. C. Goncalves, and C. J. A. Mota, Green Chem. **11**, 38 (2009).
18. J. Deutsch, A. Martin, and H. Lieske, J. Catal. **245**, 428 (2007).
19. L. Roldan, R. Mallada, J. M. Fraile, et al., Asia-Pac. J. Chem. Eng. **4**, 279 (2009).
20. A. L. Maksimov, A. I. Nekhaev, D. S. Shlyakhtitsev, et al., Neftekhimiya **50**, 339 (2010) [Pet. Chem. **50**, (2010)].
21. P. Ferreira, I. M. Fonseca, A. M. Ramos, et al., Appl. Catal. B: Environ. **98**, 94 (2010).
22. G. Vicente, J. A. Melero, G. Morales, et al., Green Chem. **12**, 899 (2010).
23. M. Kitamura, M. Isobe, Y. Ichikawa, and T. Goto, J. Am. Chem. Soc. **106**, 3252 (1984).
24. R. Albert, K. Dax, R. Pleschko, and A. E. Stuetz, Carbohydr. Res. **137**, 282 (1985).
25. P. P. Singh, M. M. Gharia, F. Dasgupta, and H. C. Srivastava, Tetrahedron Lett., 439 (1977).
26. B. Lal, R. M. Gidwani, and R. H. Rupp, Synthesis, 711 (1989).
27. C.-C. Lin, M.-D. Jan, S.-S. Weng, et al., Carbohydr. Res. **341**, 1948 (2006).

28. P. R. M. Nair, P. M. Shah, and B. Sreenivasan, Starch **33**, 384 (1981).
29. J.-I. Asakura, Y. Matsubara, and M. J. Yoshihara, Carbohydr. Chem. **15**, 231 (1996).
30. A. P. Rauter, F. Ramoa-Ribeiro, A. C. Fernandes, and J. A. Figueiredo, Tetrahedron **51**, 6529 (1995).
31. M. A. Nadtochii, L. E. Burova, I. V. Vasil'eva, and T. A. Melent'eva, Khim.-Farm. Zh. **35**, 282 (2001).
32. V. K. Rajput and B. Mukhopadhyay, Tetrahedron Lett. **47**, 5939 (2006).
33. S. N. Khadzhiev and I. M. Gerzeliev, Chem. J. March, **50**, (2010).
34. D. M. Clode, Chem. Rev. **79**, 491 (1979).
35. M. J. Climent, A. Corma, S. Iborra, et al., J. Catal. **161**, 783 (1996).
36. F. M. H. Randall and J. M. Webber, J. Chem. Soc., 3368 (1965).
37. A. Corma, M. J. Climent, H. Garcia, and J. Primo, Appl. Catal. A: Gen. **59**, 333 (1990).
38. R. Ballini, G. Bosica, B. Frullanti, et al., Tetrahedron Lett. **39**, 1615 (1998).
39. M. J. Climent, A. Velty, and A. Corma, Green Chem. **4**, 565 (2002).
40. E. E. Mallon, A. Bhan, and M. Tsapatsis, Phys. Chem. B **114**, 1939 (2010).
41. A. H. Yonli, I. Gener, and S. Mignard, Micropor. Mesopor. Mater. **132**, 37 (2010).
42. V. L. C. Goncalves, B. P. Pinto, J. C. Silva, and C. J. A. Mota, Catal. Today **133**, 673 (2008).
43. J. Tateiwa, H. Hiriuchi, and S. Uemura, J. Org. Chem. **60**, 4043 (1995).
44. G. W. Bodamer and R. Kunin, Ind. Eng. Chem. **45**, 2577 (1953).
45. A. Corma, S. Iborra, S. Miquel, and J. Prinio, J. Catal. **161**, 713 (1996).
46. J. F. Chapat, A. Finiels, J. Joffre, and C. Moreau, J. Catal. **185**, 445 (1999).
47. R. A. Sheldon and H. van Bekkum, *Fine Chemicals through Heterogeneous Catalysis* (Wiley-VCH, Weinheim, 2001).