

ORGANIC SYNTHESIS
AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis of Ethers and Cyclic Acetals in the Presence of CBV-720 Zeolite

A. V. Baiburtli, G. Z. Raskil'dina*, and S. S. Zlotskii

Ufa State Petroleum Technological University, Ufa, Bashkortostan, 450000 Russia

*e-mail: graskildina444@mail.ru

Received August 17, 2017

Abstract—CBV-720 zeolite was compared to H-Beta zeolite and KU-2 cation-exchange resin in the catalytic performance in addition of alcohols to norbornene, in condensation of aldehyde and ketone with di- and triols, and in the Prins reaction of olefins with formaldehyde. These reactions, when performed on CBV-720 zeolite, occur 1.5–2 times faster than on the other catalysts. The corresponding ethers and cyclic acetals were synthesized.

DOI: 10.1134/S1070427217070114

Acid zeolites are widely used in petrochemistry and organic synthesis, in particular, in Friedel–Crafts alkylation, alkenylation, and acylation, in transformation and functionalization of olefins and acetylenes, etc. [1–5].

On the other hand, data on the use of CBV-720 superacid zeolite in liquid-phase reactions performed under mild conditions are few [6, 7], although its successful use instead of Brønsted superacids ($\text{CF}_3\text{SO}_3\text{H}$, FSO_3H) in a number of low-temperature processes allows preparation of the desired products in high yield without using expensive and toxic solvents.

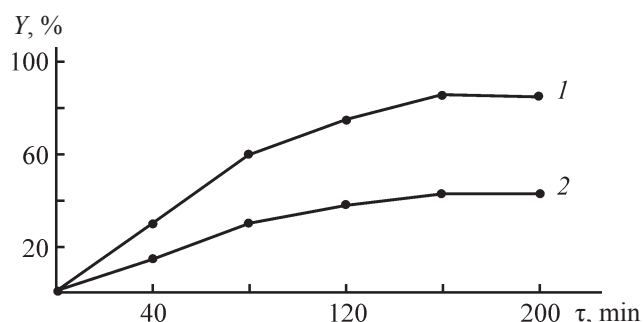
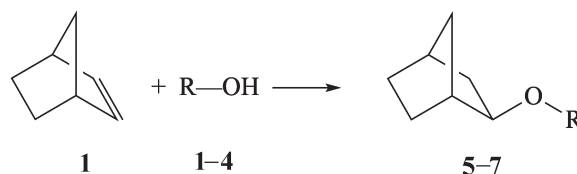


Fig. 1. Influence of the kind of the catalyst on the yield Y of ether **5**. Conditions: norbornene **1** to alcohol **2–4** molar ratio 1 : 3, 10 wt % catalyst relative to the olefin, 60–80°C, alcohol as solvent. (τ) Time; the same for Figs. 2 and 3. Zeolite: (1) CBV-720 and (2) H-Beta.

Therefore, we compared the performance of CBV-720 in common petrochemical reactions with that of the well-known heterogeneous acid catalysts such as H-Beta zeolite and KU-2 cation-exchange resin.

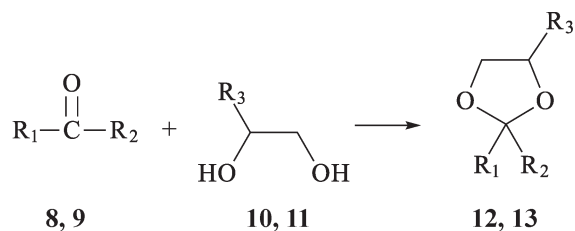
Addition of alcohols **2–4** to norbornene **1** in the presence of the chosen catalysts in the liquid phase at 60–80°C (with the alcohol also acting as solvent) yields ethers **5–7** with high selectivity:



where $R = n\text{-C}_4\text{H}_9$ (**2, 5**), $i\text{-C}_4\text{H}_9$ (**3, 6**), $i\text{-C}_3\text{H}_7$ (**4, 7**).

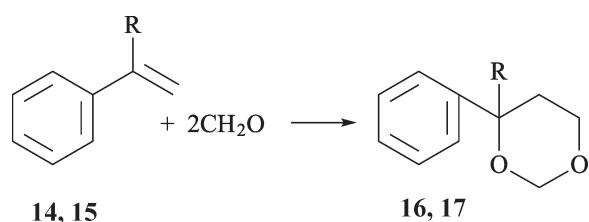
An advantage of CBV-720 zeolite is a twofold increase in the yield of butyl ether **5** relative to the yield on H-Beta zeolite (Fig. 1).

Condensation of aldehyde **8** and ketone **9** with triol **10** and diol **11** can be successfully performed in the presence of CBV-720 catalyst (Figs. 2a, 2b). At equal selectivity, the yield of heterocycles **12** and **13**, based on the carbonyl compound, with CBV-720 catalyst is 2 times higher than with H-Beta and KU-2 catalysts:



where $\text{R}_1 = \text{R}_2 = \text{CH}_3$ (**8**, **12**), $\text{R}_1 = i\text{-C}_3\text{H}_7$, $\text{R}_2 = \text{H}$ (**9**, **13**), $\text{R}_3 = \text{CH}_2\text{OH}$ (**10**, **12**), $\text{R}_3 = \text{H}$ (**11**, **13**).

Condensation of olefins **14** and **15** with formaldehyde (Prins reaction) on CBV-720 zeolite occurs 1.5–2 times faster than on H-Beta zeolite (Figs. 3a, 3b). In particular, 50% yield of 4-phenyl-1,3-dioxanes **16** and **17** is reached in 50 min on CBV-720 and in 100 min on H-Beta zeolite:



where $\text{R} = \text{H}$ (**14**, **16**), CH_3 (**15**, **17**).

It is known that the activity of zeolite catalysts and their selectivity in various reactions are determined by the acidity and pore structure of the zeolites [8, 9]. Comparison of the results of the kinetic studies suggests that the difference between the zeolite samples in the activity is caused by different accessibility of the active sites to the diffusion of the reactants. For example, higher specific surface area ($780 \text{ m}^2 \text{ g}^{-1}$) of CBV-720 zeolite ensures easier diffusion of the reactants compared to the reaction in the presence of H-Beta zeolite ($725 \text{ m}^2 \text{ g}^{-1}$), which is in agreement with the data of [6, 9].

EXPERIMENTAL

Chromatographic analysis of reaction products was performed with an HRGS 5300 Mega Series Carlo Erba chromatograph equipped with a flame ionization detector. The carrier gas was helium (flow rate 30 mL min^{-1}). The column length was 25 m, and the column temperature was $50\text{--}280^\circ\text{C}$ (programmed heating at a rate of 8 deg min^{-1}). The detector and vaporizer temperatures were 250 and 300°C , respectively. Analysis by gas chromatography–mass spectrometry

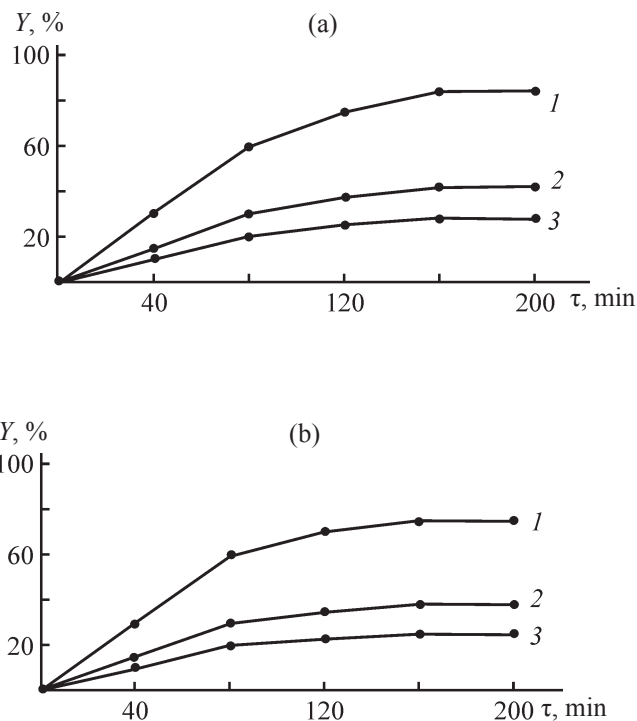


Fig. 2. Influence of the kind of the catalyst on the yield Y of compounds (a) **12** and (b) **13**. Conditions: carbonyl compound **8** or **9** to glycol **10** or **11** molar ratio 1 : 0.8, 10 wt % catalyst relative to glycol, 80°C , solvent benzene. (1) CBV-720 zeolite, (2) H-Beta zeolite, and (3) KU-2 cation-exchange resin.

was performed with Fisons (DB 560 quartz capillary column, 50 m) and Focus devices using a Finigan DSQ II mass-spectrometric detector (ion source temperature 200°C , direct inlet temperature $50\text{--}270^\circ\text{C}$, heating rate 10 deg min^{-1} , Thermo TR-5MS $50 \text{ m} \times 0.25 \text{ mm}$ column, helium flow rate 0.7 mL min^{-1}). The mass spectra were taken in the electron impact mode. The NMR spectra were recorded with a Bruker AVANCE-500 spectrometer (300.13 MHz for ^1H) from CDCl_3 solutions.

Prior to the reaction, samples of H-Beta and CBV-720 zeolites were calcined in a dry air flow at 350 and 550°C , respectively, for 5 h.

Reaction of norbornene 1 with alcohols 2–4 (general procedure). A mixture of 0.255 mol of alcohol 2–4, 0.085 mol of norbornene **1**, and 10 wt % zeolite was heated at $50\text{--}80^\circ\text{C}$ with vigorous stirring for 5 h. After the reaction completion, the catalyst was separated from the reaction mixture by filtration, and the unchanged alcohol was distilled off. The ethers were isolated by distillation at reduced pressure.

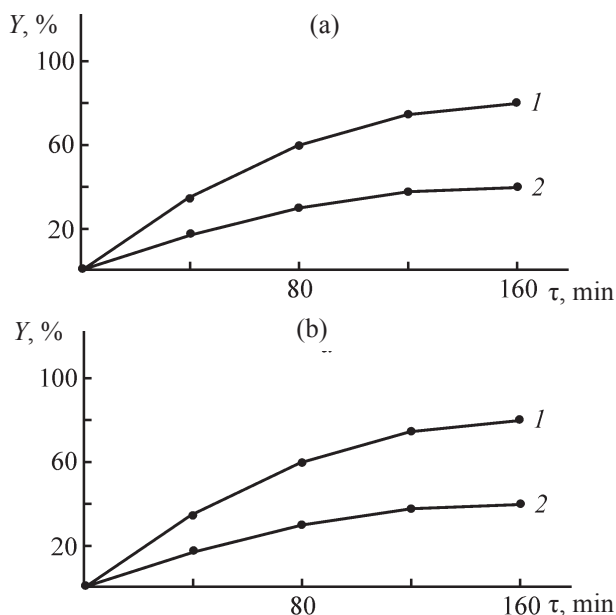


Fig. 3. Influence of the kind of the catalyst on the yield Y of compounds (a) **16** and (b) **17**. Conditions: olefin **14** or **15** to paraformaldehyde molar ratio 0.8 : 2, 10 wt % catalyst relative to olefin, 100°C, solvent 1,4-dioxane. Zeolite: (1) CBV-720 and (2) H-Beta.

The following products were obtained using this procedure.

exo-2-(Butoxy)bicyclo[2.2.1]heptane 5. The physicochemical parameters agree with the published data [10].

exo-2-(2-Methylpropoxy)bicyclo[2.2.1]heptane 6. Yield 90%, $T_b = 64^\circ\text{C}$ (12 mmHg). ^1H NMR spectrum (CDCl_3 , δ , ppm): 0.89 m (3H, CH_3), 0.99–1.06 m (2H, CH_2), 1.27–1.42 m (2H, CH_2), 1.50–1.58 m (4H, CH_2), 2.18 s (1H, CH), 2.28 s (1H, CH), 3.19–3.33 m (1H, CH), 3.19–3.33 m (2H, CH_2). ^{13}C NMR spectrum (CDCl_3 , δ_C , ppm): 21.76 (CH_3), 25.32 (CH_2), 28.71 (CH_2), 36.32 (CH_2), 37.98 (CH), 40.21 (CH_2), 43.59 (CH), 70.42 (CH), 79.02 (CH). Mass spectrum, m/e (I_{rel} , %): 154 M^+ (2), 94 (100), 79 (82), 66 (82), 67 (62), 41 (51), 43 (38), 95 (35), 83 (24), 55 (20), 68 (17), 57 (16), 112 (12), 44 (11).

exo-2-(Propoxy)bicyclo[2.2.1]heptane 7. Yield 90%, $T_b = 73^\circ\text{C}$ (12 mmHg). ^1H NMR spectrum (CDCl_3 , δ , ppm): 0.85 m (3H, CH_3), 0.98–1.08 m (2H, CH_2), 1.22–1.43 m (2H, CH_2), 1.52–1.57 m (6H, CH_2), 2.18 s (1H, CH), 2.28 s (1H, CH), 3.20–3.31 m, (1H, CH), 3.13–3.32 m (2H, CH_2). ^{13}C NMR spectrum (CDCl_3 , δ_C , ppm): 11.29 (CH_3), 25.32 (CH_2), 26.02 (CH_2), 28.71 (CH_2), 36.32 (CH_2), 37.98 (CH), 40.21 (CH_2), 43.59 (CH), 70.42 (CH_2), 79.02 (CH).

Acetalization procedure. A mixture of 0.01 mol of alcohol **10** or **11**, 0.012 mol of ketone **8** or aldehyde **9**, 10 wt % catalyst, and 30 mL of benzene was refluxed for 2–4 h up to separation of the calculated amount of water. After the reaction completion, the mixture was cooled, dried, filtered, and evaporated. Products **12** and **13** were isolated at reduced pressure.

The following products were obtained using this procedure.

2,2-Dimethyl-4-hydroxymethyl-1,3-dioxolane 12. The physicochemical parameters agree with the published data [11].

2-Isopropyl-1,3-dioxolane 13. The physicochemical parameters agree with the published data.

Reaction of olefins 14 and 15 with paraformaldehyde (general procedure). A mixture 0.1 mol of styrene **14** or α -methylstyrene **15** and 0.12 mol of paraformaldehyde in 40 mL of 1,4-dioxane in the presence of 10 wt % zeolite was stirred at the boiling point of 1,4-dioxane (100°C) for 4 h. After the reaction completion, the catalyst was filtered off, and the solvent was distilled off. Products **16** and **17** were isolated by distillation at reduced pressure.

The following products were obtained using this procedure.

4-Phenyl-1,3-dioxane 16. Yield 70%, $T_b = 94^\circ\text{C}$ (12 mmHg). ^1H NMR spectrum [CDCl_3 , δ , ppm (J , Hz)]: 1.39–1.43 m (2H, CH_2), 3.64–3.75 m (2H, CH_2), 4.03 t (1H, CH, J 2.1), 5.02 d (2H, CH_2 , J 4.8), 7.22–7.39 m (5H, Ph–). ^{13}C NMR spectrum (CDCl_3 , δ_C , ppm): 33.76 (CH_2), 68.42 (CH_2), 77.03 (CH), 96.49 (CH_2), 120.82–142.82 (Ph–). Mass spectrum, m/e (I_{rel} , %): 86 (50), 71 (20), 57 (100), 43 (29).

4-Methyl-4-phenyl-1,3-dioxane 17. Yield 80%, $T_b = 121^\circ\text{C}$ (12 mmHg). ^1H NMR spectrum [CDCl_3 , δ , ppm (J , Hz)]: 1.32 s (3H, CH_3), 1.60–1.68 m (2H, CH_2), 3.67–3.71 m (2H, CH_2), 5.02 d (2H, CH_2 , J 4.6), 7.20–7.45 m (5H, Ph–). ^{13}C NMR spectrum (CDCl_3 , δ_C , ppm): 25.11 (CH_3), 35.55 (CH_2), 69.44 (CH_2), 77.61 (C), 93.77 (CH_2), 120.62–138.67 (Ph–). Mass spectrum, m/e (I_{rel} , %): 163 (30), 132 (24), 117 (26), 105 (100), 91 (28), 77 (29).

CONCLUSIONS

CBV-720 zeolite surpasses H-Beta zeolite and KU-2 cation-exchange resin in the catalytic performance in

addition of alcohols to norbornene, in condensation of aldehyde and ketone with di- and triol, and in the Prins reaction of olefins with formaldehyde. The corresponding ethers and cyclic acetals were successfully prepared in the presence of CBV-720 zeolite.

ACKNOWLEDGMENTS

The authors are grateful to Prof. A.V. Vasil'ev for the support and assistance in the study.

The study was financially supported by the Russian Science Foundation (project no. 15-13-10034).

REFERENCES

1. *Zeolite Chemistry and Catalysis: ACS Monograph no. 171*, Rabo, J.A., Ed., Am. Chem. Soc., 1976.
2. Raskil'dina, G.Z., Grigor'eva, N.G., Kutepov, B.I., and Zlotskii, S.S., *Uspekhi organicheskogo sinteza na tseolitakh* (Advances in Organic Synthesis on Zeolites), Lambert Academic, 2014, p. 100.
3. Smith, K. and El-Hiti, G.A., *Green Chem.*, 2011, vol. 13, pp. 1579–1608.
4. Wang, W. and Hunger, M., *Acc. Chem. Res.*, 2008, vol. 41, pp. 895–904.
5. Ramazanov, D.N., Dzhumbe, A., Nekhaev, A.I., et al., *Petrol. Chem.*, 2015, vol. 55, no. 2, pp. 140–145.
6. Ryabukhin, D.S. and Vasilyev, A.V., *Tetrahedron Lett.*, 2015, vol. 56, pp. 2200–2202.
7. Boyarskiy, V.P., Ryabukhin, D.S., Bokach, N.A., and Vasilyev, A.V., *Chem. Rev.*, 2016, vol. 116, no. 10, pp. 5894–5986.
8. Kubasov, A.A., *Soros. Obraz. Zh.*, 1998, no. 7, pp. 70–76.
9. Bogdan, V.I., Koklin, A.E., and Kazanskii, V.B., *Kinet. Catal.*, 2010, vol. 51, no. 5, pp. 736–742.
10. Raskil'dina, G.Z., Suleimanova, A.M., Kazakova, A.N., et al., *Petrol. Chem.*, 2015, vol. 55, no. 2, pp. 154–162.
11. Valiev, V.F., Raskil'dina, G.Z., Mudrik, T.P., et al., *Bashk. Khim. Zh.*, 2014, vol. 21, no. 3, pp. 25–27.