Dimerization and oligomerization of styrene in the presence of pentasils*

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Styrene is converted to dimers under the action of zeolite ZSM-12 both in the presence and absence of the solvent (chlorobenzene). This transformation is characterized by a high conversion of the monomer (up to 100 wt.%) and selective formation of linear isomers (70—75%). In the presence of zeolites ZVN and VKZ in chlorobenzene, styrene forms a mixture of oligomers (n = 2—7), among which the dimers prevailed, while without the solvent oligomers with an average molecular weight of ~1510 are formed.

Key words: styrene, oligomerization, dimerization in bulk, dimerization in solvent, cyclic and linear dimers, oligomers, zeolites, pentasils.

Styrene dimers are promising as regulators of polymer chain growth, plasticizers of polymers and Plexiglas, a basis of synthetic lubricants, and components of epoxide, varnish-and-paint, and poly(vinyl chloride) materials.[1—4] Strong acids, namely, $AcClO_4$, CF_3SO_3H, and p-$MeC_6H_4SO_3H$ are usually used[5—7] for the synthesis of styrene dimers, although it is shown[8,9] that zeolites Y and Beta are highly active in styrene dimerization. The linear dimer of styrene, *viz.*, (*E*)-1,3-diphenylbut-1-ene, was obtained with the selectivity up to 80% in the presence of zeolite Y at 70 °C, whereas zeolite Beta is more selective (84—90%) with respect to the formation of cyclic styrene dimers: *cis*- and *trans*-1-methyl-3-phenylindanes.

The use of pentasils in styrene dimerization is unknown. Since these zeolites possess[10] stronger acid sites than zeolites Y and Beta, it was of interest to study the catalytic properties of the pentasils in styrene dimerization.

In the present work, we studied the transformations of styrene in the presence of pentasils of two different structural types: MTW (zeolite ZSM-12) and MFI (zeolites ZVN[11,12] and VKZ[13,14]). The data obtained on the activity and selectivity of the catalysts in styrene dimerization were compared to their acidic properties and molecular-sieve characteristics.

Experimental

Samples of the pentasils in the H-form were studied: industrial catalysts ZSM-12 (SiO_2/Al_2O_3 = 34) and ZVN (SiO_2/Al_2O_3 = 28) produced at the OAO "Angarskii zavod katalizatorov i organicheskogo sinteza" and VKZ (SiO_2/Al_2O_3 = 40) synthesized by the hydrothermal method from alkaline aluminosilicate gel using hexamethylenediamine as an organic additive.

Before experiments on styrene oligomerization, the catalyst samples were heated in air for 4 h at 540 °C. Styrene (OAO "Salavatnefteorgsintez") were distilled. Chlorobenzene was dehydrated using a standard method.

Styrene oligomerization was carried out in a periodical isothermal reactor at 80—130 °C in the presence of 5—40 wt.% catalyst in chlorobenzene and without a solvent. The initial styrene concentration in chlorobenzene $[M]_0$ was 2.2 mol L^{-1}.

^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-400 spectrometer (^1H, 400.13 MHz; ^{13}C, 100.62 MHz) in $CDCl_3$. High-resolution mass spectra were measured on a Fisons Trio 1000 instrument, whose chromatograph was equipped with a DB 560 quartz column (50 m); the temperature of the column was increased from 50 to 320 °C with a programmed heating rate of 4 °C min^{-1}; electron impact (70 eV). GLC analysis was carried out on an HRGS 5300 Mega Series chromatograph (Carlo Erba) with a flame-ionization detector (capillary column 25 m, SE-30 phase, temperature-programmed heating from 50 to 280 °C at a rate of 8 °C min^{-1}, detector temperature 250 °C, evaporator temperature 300 °C, helium as a carrier gas, 30 mL min^{-1}). Analysis by high-performance liquid chromatography (HPLC) was performed on an HP-1090 chromatograph with a refractometric detector and a Plgel 100 Å polystyrene column using toluene as an eluent, a toluene flow rate of 0.8 mL min^{-1}, and a tape velocity of 1.5 cm min^{-1}.

The current concentration of styrene and quantitative composition of the dimeric fraction were determined by GLC. The time of dimer elution (min) was as follows: (*Z*)-1,3-diphenylbut-1-ene, 15.2; *cis*-1-methyl-3-phenylindane, 15.6; *trans*-1-methyl-3-phenylindane, 15.9; (*E*)-1,3-diphenylbut-

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1-ene, 17.1. The time of elution of trimers ranged from 26.2 to 28.4 min (12 peaks).

For the identification of the styrene dimers, the cyclic dimer 1-methyl-3-phenylindane was synthesized as a mixture of two isomers according to an earlier described procedure.[15] Linear dimers were identified in a mixture of all the four isomers with the following compositions (wt.%): (*Z*)-1,3-diphenylbut-1-ene (**1a**), 1.7; (*E*)-1,3-diphenylbut-1-ene (**1b**), 74.1; *cis*-1-methyl-3-phenylindane (**2a**), 10.9; *trans*-1-methyl-3-phenylindane (**2b**), 13.3.

The molecular-weight distribution of products of styrene oligomerization was determined by HPLC. Styrene dimers and trimers were isolated by vacuum distillation for calibration. The molecular weights of the dimers and trimers and the high-molecular-weight fraction with the degree of oligomerization $n = 14$ were determined by Rast´s method.[16] The other n-mers were determined by the polystyrene calibration, which was carried out by the standards obtained from Aldrich.

1,3-Diphenylbut-1,2-enes (1a,b). The ^{1}H NMR spectrum of the mixture contained a group of overlapped signals from the isomers, δ: 7.50—7.80 (m, H arom.). (*Z*)-Isomer (**1a**). ^{1}H NMR, characteristic signals, δ: 1.75 (d, 3 H, Me); 4.35 (m, 1 H, CH); 6.84, 7.0 (both m, 1 H each, =CH). ^{13}C NMR, characteristic signals, δ: 23.2 (Me), 38.1 (C(3)$_{\text{butene}}$), 129.9 (C(1)$_{\text{butene}}$), 137.3 (C(2)$_{\text{butene}}$). MS, m/z (I_{rel} (%)): 208 (44.6), Kovač index I_{k} 1687. (*E*)-Isomer (**1b**). ^{1}H NMR, characteristic signals, δ: 1.85 (d, 3 H, Me); 4.0 (q, 1 H, CH); 6.77 (m, 1 H, =CH, J = 16 Hz); 6.81 (d, 1 H, =CH, J = 16 Hz). ^{13}C NMR, characteristic signals, δ: 21.5 (Me), 42.9 (C(3)$_{\text{butene}}$), 127.4 (C(1)$_{\text{butene}}$), 135.56 (C(2)$_{\text{butene}}$). MS, m/z (I_{rel} (%)): 208 (64.6), Kovač index I_{k} 1795. The spectral characteristics are close to those described in literature.[17]

1-Methyl-3-phenylindanes (2a,b). The ^{1}H NMR spectrum of the mixture contained a group of overlapped signals from the isomers, δ: 7.50—7.80 (m, 9 H, H arom.). *cis*-Isomer (**2a**). ^{1}H NMR, characteristic signals, δ: 1.78 (d, 3 H, Me); 1.93, 2.99 (both m, 1 H each, CH$_2$); 3.50 (m, 1 H, CHMe); 4.52 (t, 1 H, CHPh). ^{13}C NMR, characteristic signals, δ: 19.5 (Me), 38.6 (C(1)), 46.9 (C(2)), 50.9 (C(3)). MS, m/z (I_{rel} (%)): 208 (85.3), Kovač index I_{k} 1702. *trans*-Isomer (**2b**). ^{1}H NMR, characteristic signals, δ: 1.69 (d, 3 H, Me); 2.49, 2.61 (both m, 1 H each, CH$_2$); 3.68 (q, 1 H, CHMe); 4.73 (t, 1 H, CHPh). ^{13}C NMR, characteristic signals, δ: 20.8 (Me), 38.4 (C(1)), 45.0 (C(2)), 49.9 (C(3)). MS, m/z (I_{rel} (%)): 208 (100), Kovač index I_{k} 1719. The spectral characteristics are close to those described in literature.[18]

Results and Discussion

Oligomerization of styrene in the presence of the pentasils occurs with the formation of the dimers of (*Z*)- (**1a**), (*E*)-1,3-diphenylbut-1-ene (**1b**), *cis*- (**2a**) and *trans*-1-methyl-3-phenylindane (**2b**) (Scheme 1) and higher-molecular-weight oligomers.

The composition and yield of the reaction products depend substantially on the structural type of pentasil and reaction conditions, and specifically whether the oligomerization occurs in solution or in bulk.

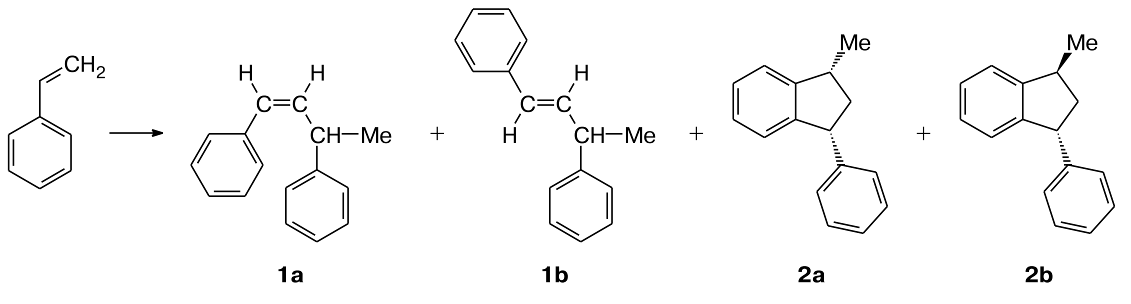
High-molecular-weight compounds with a molecular weight of ~1510 are formed in the absence of solvent under the action of zeolites ZVN and VKZ (20 wt.%, 110 °C). The catalyst is rapidly deactivated by the oligomers formed and, hence, the conversion of styrene is not high: 20—35 wt.% (Fig. 1, *a*, *b*).

Unlike this, styrene oligomerization in the bulk in the presence of zeolite ZSM-12 occurs with the styrene conversion higher than 90 wt.%. The dimers are predominantly formed (80%), and the amount of higher-molecular-weight oligomers is small and the degree of oligomerization is restricted by tetramers (Fig. 1, *c*). The fraction of linear isomers among the dimers is 75%. The (*Z*)-isomer of 1,3-diphenylbut-1-ene (**1a**) is formed in considerable amounts (up to 10%) in the presence of zeolite ZSM-12, whereas only a more stable (*E*)-isomer (**1b**) was identified on the other zeolites.

The results of styrene oligomerization in a chlorobenzene solution (20 wt.% catalyst, 110 °C, $[\mathrm{M}]_0 = 2.2$ mol L^{-1}) in the presence of the pentasils are shown in Figs 1, *a*—*c*. It is seen that zeolite ZSM-12 manifests the maximum activity in the reaction, while on zeolites VKZ and ZVN the styrene conversion is considerably lower: 61.0 and 28.0 wt.%, respectively.

The differences observed in the catalytic activity are not related to the acidic properties of the pentasils, because the strength of the Brönsted acid sites (BAS) in these catalysts is the same (1165 kJ mol^{-1}) and the BAS concentration in zeolite ZVN is even higher than that in zeolite ZSM-12 (135 and 106 μmol g^{-1}, respectively).[19]

Scheme 1



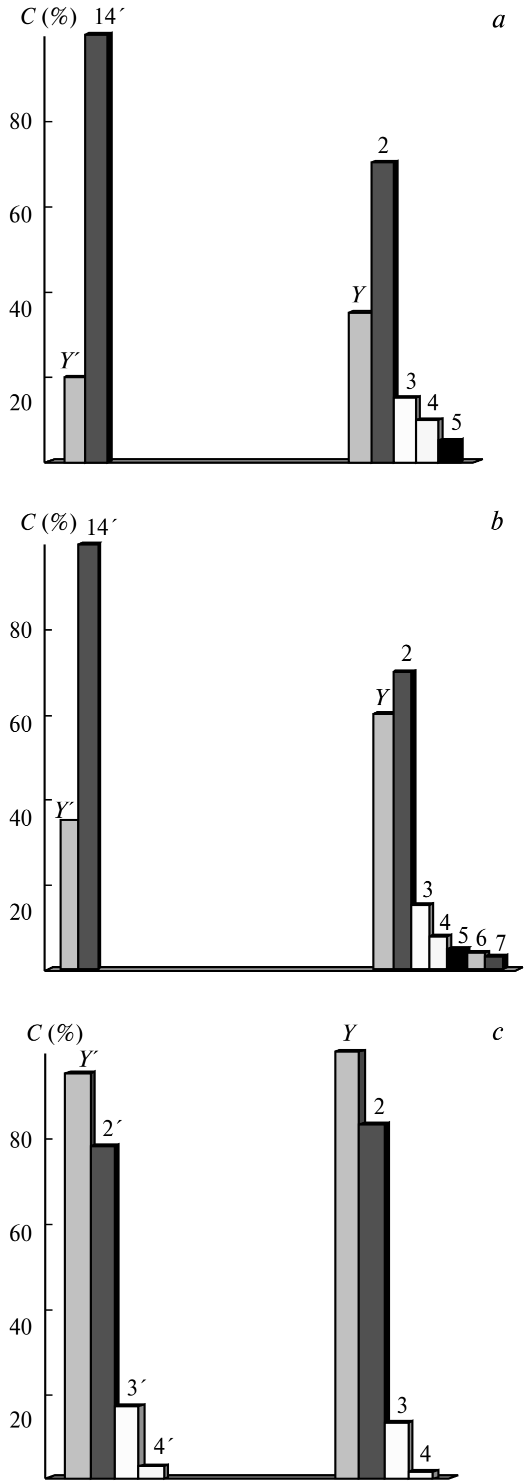


Fig. 1. Conversion of styrene and molecular-weight distribution of the oligomers in chlorobenzene and without solvent (symbols with hachures) formed in the presence of pentasils (20 wt.% catalyst, 110 °C, $[M]_0 = 2.2$ mol L^{-1}, 1 h): ZVN (*a*), VKZ (*b*), and ZSM-12 (*c*); *Y* is the styrene conversion; 2, 3, 4, 5, 6, 7, and 14 is the selectivity of formation of the di-, tri-, tetra-, penta-, hexa-, hepta-, and 14-mers, respectively.

In addition, it is known that within the same structural type of zeolites an increase in the SiO_2/Al_2O_3 molar ratio (M) induces a decrease in the concentration of acid sites and, therefore, the activity of zeolite VKZ ($M = 40$) in the reaction should be lower than that in the case of zeolite ZVN ($M = 28$). In fact we observe an opposite situation: the styrene conversion in the presence of zeolite VKZ is by 2—3 times higher than that in the presence of zeolite ZVN. The low activity of the pentasils with the MFI structure in styrene dimerization is caused by specific features of their framework topologies. The sizes of pores in zeolites of the MFI type (equidimensional tubes with a diameter of 0.56 nm and sinusoidal channels with a diameter of the aperture of 0.51×0.55 nm) make it possible the dimers to form but impede substantially diffusion of products from the pores. Therefore, styrene oligomerization in the presence of zeolites of the MFI type involves, most likely, the surface acid sites, accounting for 30% of the total number of BAS.[20]

Oligomers with a broad molecular-weight distribution ($n = 2$—5 on zeolite VKZ and $n = 2$—7 on zeolite ZVN) are formed under the action of pentasils of the MFI type. This also can confirm that the reaction occurs on the external catalyst surface that contains no steric restrictions for chain growth. Predominantly cyclic dimers **2a**,**b** (ratio **1** : **2** = 38 : 62) are formed on the VKZ zeolite, whereas linear dimer **1b** (ratio **1** : **2** = 67 : 33) is formed on zeolite ZVN.

Compared to zeolites ZVN and VKZ, the system of pores in zeolite ZSM-12 is formed by broad straight channels (the diameter of the aperture is 0.56×0.59 nm), which favors the removal of the formed oligomer molecules from the catalyst channels. At the same time, the sizes of channels of zeolite ZSM-12 restrict the formation of molecules with the degree of oligomerization $n \geq 3$. As a result, the major products of styrene conversion on zeolite ZSM-12 are dimers (up to 83.0%), among which linear isomers **1a**,**b** predominate (the ratio **1** : **2** is 78 : 22). Minor amounts of trimers (up to 15.0%) and tetramers (1.5—2.0%) are formed on the surface active sites.

The ratio of the products varies, depending on the reaction conditions (Fig. 2). An increase in the temperature (80—130 °C) and catalyst amount (5—40 wt.%) decreases the fraction of linear isomers **1a**,**b** in the composition of the dimers and increases the amount of cyclic dimers **2a**,**b**. The amount of tri- and tetramers increases insignificantly.

Isomeric composition of the styrene dimers in the presence of zeolites ZSM-12 and ZVN as a function of the reaction time is given in Table 1. The starting product was the fraction isolated by vacuum distillation. The fraction had the following composition: 9.6 wt.% cyclic dimers **2a**,**b** and 90.4 wt.% linear isomers **1a**,**b**. As can be seen, in the presence of both catalysts, the amount of both (Z)- and (E)-isomers of linear dimers decreases due to intramolecular ring closure (Scheme 2).

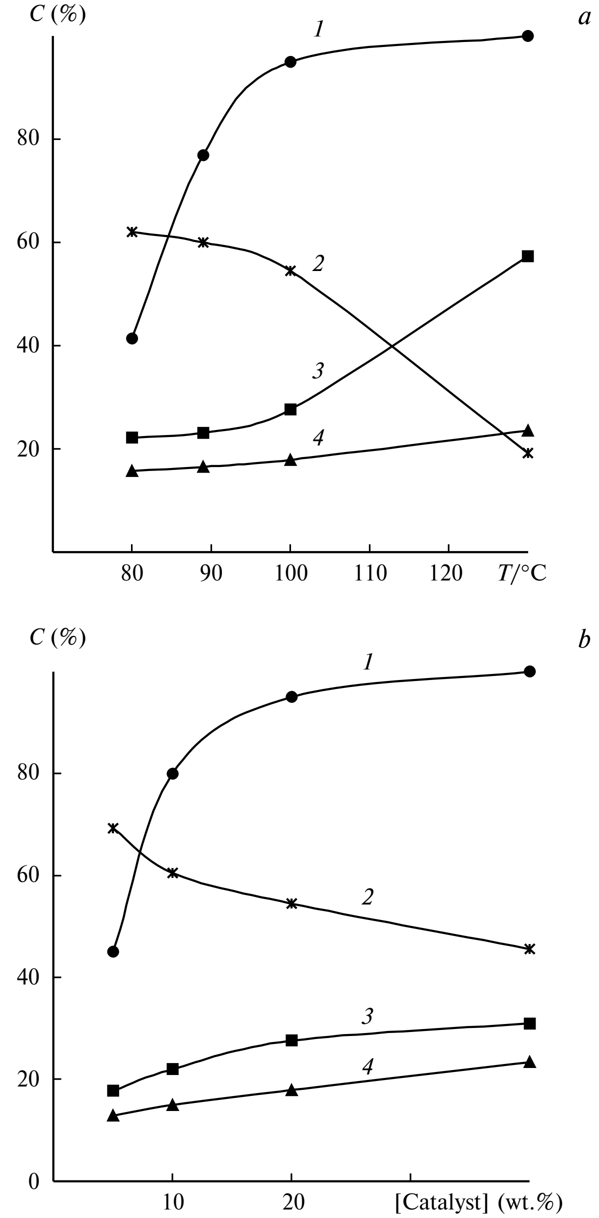


Fig. 2. Influence of the reaction parameters on the styrene conversion and selectivity of formation of the reaction products in the presence of zeolite ZSM-12 in chlorobenzene: *1*, styrene conversion; *2*, *3*, and *4*, selectivity of formation of compounds **1** and **2** and oligomers with $n = 3—4$, respectively; (*a*) 20 wt.% catalyst, $[M]_0 = 2.2$ mol L^{-1}, 1 h; (*b*) 110 °C, $[M]_0 = 2.2$ mol L^{-1}, 1 h.

As a result, the ratio **1** : **2** changes from 90 : 10 to 87 : 13 (on zeolite ZSM-12). The ring closure rate is lower in the presence of zeolite ZVN.

In addition to the increase in the amount of cyclic dimers, the ratio of *cis*/*trans* isomers (**2a**/**2b** = 1.07—1.17) also changes compared to the starting product (**2a**/**2b** = 0.92). The formation of *cis*-isomer **2a** is considered[6] to be thermodynamically more favorable, because only in this conformation the both substituents can be in the equatorial position relative to the indane ring.

Scheme 2

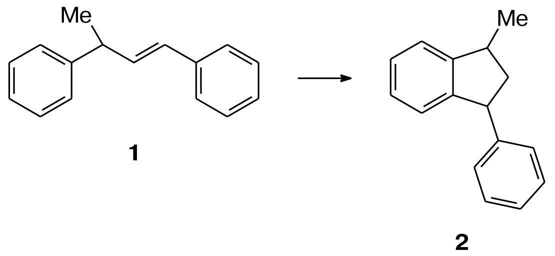


Table 1. Isomeric composition of the styrene dimers under the action of zeolites ZSM-12 and ZVN as a function of the reaction time ($T = 110$ °C, 20 wt.% catalyst)

Catalyst	*t*/h	**2a**/**2b**	Isomeric composition (wt.%)				**1** : **2**
			2a	**2b**	**1b**	**1a**	
Initial composition	0	0.92	4.6	5.0	88.4	2.0	90 : 10
ZSM-12	1	1.07	6.2	5.8	86.7	1.3	88 : 12
	3	1.11	6.8	6.1	85.7	1.4	87 : 13
	5	1.08	6.7	6.2	85.7	1.4	87 : 13
ZVN	2	1.17	6.3	5.4	87.4	0.9	88 : 12
	5	1.13	6.1	5.4	87.5	1.0	88 : 12
	7	1.07	6.1	5.7	87.2	1.0	88 : 12

Thus, due to an optimum combination of the acidic properties and molecular-weight characteristics, the use of zeolite ZSM-12 makes it possible to perform the dimerization of styrene both with and without solvent with a high selectivity of formation of linear dimers (70—75%) and the monomer conversion up to 100 wt.%.

In the presence of zeolites VKZ and ZVN, styrene oligomerization in the bulk affords oligomers with a molecular weight of ~1510, and a mixture of oligomers ($n = 2—7$) with the predomination of dimers is formed in chlorobenzene. The low activity and selectivity of these zeolites are due to the fact that the reaction occurs on the external catalyst surface.

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