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Styrene Oligomerization Catalyzed by Zeolites of Different Structural Types

**N. G. Grigor'eva, R. R. Talipova, L. Ph. Korzhova, S. V. Bubennov,
B. I. Kutepov, and U. M. Dzhemilev**

Institute of Petroleum Chemistry and Catalysis, Russian Academy of Sciences, Ufa, Russia
e-mail: grig-ng@mail.ru

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Abstract—It was shown that styrene oligomerization in the presence of the zeolite ZSM-12 in a solvent (chlorobenzene) as well as without it proceeds with a high conversion (98–100 wt %) and a high selectivity for linear dimers (up to 82%). The main oligomerization products in the presence of the zeolite Beta are dimers (70–80%), mostly the linear isomer *trans*-1,3-diphenylbut-1-ene. In the presence of the less active zeolite Y, styrene gives a complex mixture of oligomers in which dimers (53–60%, in chlorobenzene) or dimers and trimers (60–80%, in bulk) are predominant.

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It is known that styrene forms linear (*trans*-1,3-diphenylbut-1-ene, **Ia**) and cyclic (*cis*- and *trans*-isomers of 1-methyl-3-phenylindane, **IIa**, **IIb**) dimers, as well as a large amount of oligomers, in the presence of acid catalysts [1–5].

The dimers of styrene can be applied as regulators for controlling the molecular weights of various polymers [6], plasticizers [7], a base stock of synthetic lubricants [8, 9], and components of epoxy resins and paint-and-varnish materials [10].

For the synthesis of dimers with a 90% or higher selectivity, it was proposed [4, 11–13] to carry out the reaction in the presence of strong acids, such as CF_3SO_3H and $AcClO_4$. Similar results were obtained with the use of zeolites Y and Beta [14, 15]. For example, the linear dimer was synthesized with a selectivity of 81% in the presence of zeolite Y with a degree of proton exchange of 10% (55 wt % of the catalyst, concentration of styrene in CH_2Cl_2 0.2 mol/l, 25°C), [14] and the cyclic dimers were obtained with a selectivity of 84–90% on zeolite Beta (500–1000 wt % of the catalyst, concentration of styrene in CCl_4 0.02 mol/l, 72°C) [15].

It should be pointed out that the synthesis of the styrene linear dimer is performed in the presence of large amounts of both the catalyst and solvent, which considerably decreases the preparative value of the method. As there are no comments in the published works regarding the choice of reaction conditions, it can be assumed that such reaction parameters are caused by the low activity of the catalysts or their fast deactivation by the resulting products.

The goal of our work is the development of effective zeolite catalysts of various structural types, which would make it possible to carry out linear and cyclic styrene dimerization selectively and under mild conditions.

EXPERIMENTAL

The following zeolites in their H forms were investigated in the present work: Y (SiO_2/Al_2O_3 = 6.0; Na^+/H^+ ion exchange degree 96%) synthesized according to the procedure described in [16], Beta (SiO_2/Al_2O_3 = 18), and ZSM-12 (SiO_2/Al_2O_3 = 34) produced by OAO Angarsk Plant of Catalysts and Organic Synthesis. The samples of the catalysts were precalcined in an air atmosphere for 4 h at 540°C. Styrene was distilled prior to use, its purity was 99.0 wt %.

The oligomerization of styrene was carried out in an isothermal batch reactor at 80–120°C in the presence of 5–30 wt % of the zeolite catalysts in chlorobenzene as well as without a solvent. The initial concentration of styrene in chlorobenzene $[M]_0$ was varied from 0.88 to 8.8 mol/l.

The current styrene concentration and quantitative composition of the dimers were determined by GLC analysis with a Carlo Erba HRGS 5300 Mega Series chromatograph equipped with a flame-ionization detector: 25-m glass capillary column, stationary phase SE-30, column temperature 50–280°C (8°C/min), detector temperature 250°C, vaporizer temperature 300°C, and helium as the carrier gas (30 ml/min). The retention times (min) for the dimers were as follows: *cis*-1,3-diphenylbut-1-ene, 15.2; *cis*-1-methyl-3-phenylindane, 15.6; *trans*-1-methyl-3-phenylindane, 15.9; and *trans*-1,3-diphenylbut-1-ene, 17.1; the retention times of the trimers were 26.2–28.4 (12 peaks).

Table 1. Bulk oligomerization of styrene in the presence of different zeolites

Catalyst	Reaction conditions			Styrene conversion, wt %	Oligomer composition, wt %					I : II ratio
	[kt], wt %	T, °C	time, h		$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 14$	
Y	5	110	1	18.5	37.3	25.0	11.1	4.1	22.5	60 : 40
	10	80	1	16.0	18.6	12.2	8.1	2.9	58.2	58 : 42
	10	110	1	20.9	50.8	32.5	10.1	2.3	4.3	55 : 45
Beta	10	110	1	68.9	69.0	24.0	5.1	1.9	–	65 : 35
ZSM-12	10	110	1	82.5	79.3	20.2	0.5	–	–	77 : 23

[kt] – catalyst concentration, % of styrene mass.

The identification of the styrene dimers was performed by GC–MS analysis, as well as by a comparison of the resulting data with those known from published data [14]. The analysis was carried out with an FISONS TRIO 1000 instrument under the following conditions: GC: column temperature, 50–320°C (4°C/min), vaporizer temperature 260°C, helium as the carrier gas (1 cm^3/min), split ratio 1 : 100; MS in EI mode: source temperature 200°C, 70 eV; and MS in Cl$^+$ mode: source temperature 150°C, methane as the reagent gas. The EI mass spectra of the styrene dimers, m/z (intensity): *trans*-1,3-diphenylbut-1-ene (**Ia**)—Ik 1795: 209 (11.6); 208 (64.6); 193 (62.8); 178 (30.9); 130 (23.8); 115 (100); 91 (37.7); *cis*-1,3-diphenylbut-1-ene (**Ib**)—Ik 1687: 209 (8.1); 208 (44.6); 193 (50.1); 178 (26.5); 130 (23.9); 115 (100); 91 (39.3); *cis*-1-methyl-3-phenylindane (**IIa**)—Ik 1702: 209 (15.1); 208 (85.3); 207 (17.9); 193 (56.9); 178 (39.7); 130 (100); 115 (75.8); *trans*-1-methyl-3-phenylindane (**IIb**)—Ik 1719: 209 (18.1); 208 (100); 207 (25.5); 193 (69.6); 178 (47.0); 130 (85.5); 115 (80.8). The Cl$^+$ mass-spectra of the styrene dimers, m/z (intensity): **Ia**—Ik 1795: 209 (33.82); 208 (12.39); 207 (3.25); **Ib**—Ik 1687: 209 (1.38); 208 (5.14); 207 (1.37); **IIa**—Ik 1702: 209 (4.03); 208 (7.02); 207 (7.31); **IIb**—Ik 1719: 209 (4.68); 208 (7.97); 207 (8.02). It is known that when both of the isomers are present, the mass spectra of the *cis*- and *trans*-isomers can be distinguished: as a rule, the molecular ion is more abundant in the spectrum of the *trans*-isomer [17]. The influence of alkene stereochemistry on the abundance of (M + H)$^+$ ions is most clearly displayed in chemical ionization (Cl$^+$) mass spectra. The peaks of these ions are more intensive for *trans*-isomers than for *cis*-isomers [18].

The MMD of the styrene oligomers was determined by HPLC analysis with an HP-1090 chromatograph fitted with the polystyrene column PI gel 100 Å and a refractive index detector; toluene flow rate 0.8 ml/min, recorder speed 1.5 cm^{-1}.

For calibration, the styrene dimers and trimers were isolated by vacuum distillation. Their molecular weights as well as the molecular weights of oligomers with a polymerization degree of $n = 14$ were determined by Rast's method [19]. The other n-mers were analyzed by using the polystyrene calibration performed in accordance with the Aldrich standards.

RESULTS AND DISCUSSION

The bulk (solvent-free) oligomerization of styrene in the presence of zeolites leads to a complex mixture of oligomers (Table 1), in contrast to its closest structural analogue α-methylstyrene, which predominantly gives dimers under the same conditions [20, 21]. It is seen from the presented results that the activity of the catalysts in the reaction increases in the order: Y < Beta < ZSM-12.

Zeolite Y promotes the formation of an oligomeric product having a bimodal MMD. In the low-molecular part (oligomerization degree $n = 2$–5), the styrene dimers prevail, whereas the high-molecular fraction contains oligomers with a molecular weight of 1510. The yield of these oligomers increases with a decrease in the temperature from 110 to 80°C or in the catalyst concentration from 10 to 5 wt %.

The oligomers prepared in the presence of the high-silica zeolites Beta and ZSM-12 are characterized by a narrower MMD ($n = 2$–5 and 2–4, respectively), the percentage of the dimers in them increases to 69–79.3 wt %.

It should be noted that in the presence of zeolites Y and Beta, the *trans*-isomer of 1,3-diphenylbut-1-ene (**Ia**) was mostly obtained; only traces of the *cis*-isomer (**Ib**) of the linear dimer were present. On zeolite ZSM-12, the amount of the *cis*-isomer (**Ib**) reached 10 wt %.

The comparison of the isomeric composition of the dimers obtained in the presence of different zeolites shows that the ratio between the cyclic and linear isomers **II** : **I** changes towards an increase in the amount of linear dimers on passing from zeolite Y to zeolite ZSM-12, i.e., with a decrease of the crystal lattice pore size.

The results of styrene oligomerization in a solvent (chlorobenzene) at various initial concentrations of the monomer $[M]_0$ are presented in Fig. 1. It has been found that, as in the experiments without a solvent, zeolites ZSM-12 and Beta exhibit the highest activity. The activity of the zeolite Y is considerably lower (Fig. 1a). A decrease in the initial monomer concen-

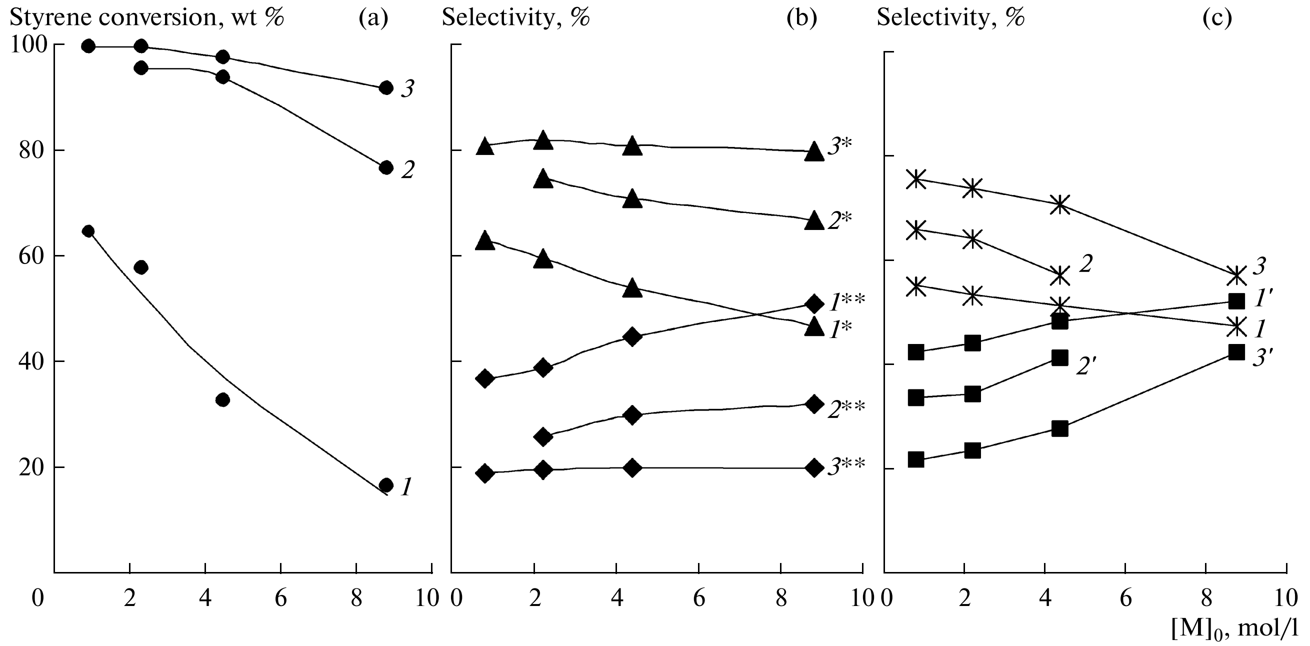

Fig. 1. Influence of the initial styrene concentration $[M]_0$ on (a) styrene conversion, (b) selectivity for dimers and oligomers, and (c) selectivity for linear and cyclic dimers in the presence of zeolites (*1*) Y, (*2*) Beta, and (*3*) ZSM-12; reaction conditions: 20 wt % of catalyst, 110°C, 1 h. (*1–3*) Linear dimers, (*1'–3'*) cyclic dimers, (*1*–3**) total dimers, and (*1**–3***) oligomers.

tration $[M]_0$ in chlorobenzene from 8.8 to 0.88 mol/l leads to an increase in the styrene conversion. The influence of the abovementioned factor on the rate of styrene oligomerization is particularly noticeable in the presence of zeolite Y.

The styrene oligomerization catalyzed by zeolite Y in the solvent gives mostly dimers and trimers (83–95 wt %), the maximal degree of oligomerization is $n = 5$, but the amount of pentamers does not exceed 2%. The total yield of dimers increases from 47 to 64% with a decrease in the monomer concentration $[M]_0$ and the proportion of linear dimers among them increases from 51 to 56 wt % (Figs. 1b, 1c).

A similar dependence has been obtained for zeolite Beta, although the dimer formation selectivity and, in particular, that of the linear isomer is higher: 67–75 wt % for dimers and 58–66 wt % for the linear isomer **Ia** (Figs. 1b, 1c).

A decrease in the initial monomer concentration $[M]_0$ in chlorobenzene from 8.8 to 0.8 mol/l has a negligible influence on the styrene conversion in the presence of zeolite ZSM-12 as well as on the oligomer composition. Thus, the styrene conversion increases from 90 to 99% (Fig. 1a) and the amount of dimers and oligomers with $n \geq 3$ remains almost unchanged (Fig. 1b). The isomeric composition of the dimers is changed: with a decrease in the concentration $[M]_0$ in chlorobenzene, the linear dimer formation selectivity increases (from 55% at $[M]_0 = 8.8$ mol/l to 78% at $[M]_0 = 0.88$ mol/l) (Fig. 1c).

Studying styrene polymerization in dichloroethane in the presence of H_2SO_4, Jenkinson and Pepper [22] found that the addition of *tert*-butanol led to the termination of oligomer chains, resulting in products with smaller molecular masses. We have tried to use this approach in order to increase the dimer formation selectivity in the presence of zeolite Y. It has been found that the admixture of 0.5 wt % *tert*-butanol leads to an increase in the selectivity for the linear dimer—the **Ia** : **II** ratio changes from 63 : 37 (without alcohol) to 70 : 30 (20 wt % of the catalyst, 110°C, $[M]_0 = 2.2$ mol/l). In addition, the MMD of oligomers narrows: the products contain only dimers and trimers. At the same time, the styrene conversion drops by 30% and side products appear, which are codimers of styrene and isobutylene formed as a result of the alcohol dehydration.

The investigation into the influence of the catalyst concentration and temperature on the styrene conversion and composition of oligomers has shown (Table 2) that a high monomer conversion (90–99%) is reached at 100–110°C over zeolites Beta and ZSM-12 taken in an amount of 10–20%. Under the same conditions, zeolite Y is less active: the styrene conversion over it does not exceed 60 wt %.

The change in the reaction parameters does not have a considerable effect on the constitution of the oligomers. With an increase in the temperature and catalyst concentration, the rate of the intramolecular alkylation rises and, as a result, the selectivity for linear dimers decreases whereas that for the cyclic dimers increases (Figs. 2a, 2b).

Table 2. Influence of the catalyst concentration and reaction temperature on the styrene conversion and product composition ($[M]_0 = 2.2$ mol/l, 1 h)

Catalyst	Reaction conditions		Styrene conversion, wt %	Oligomer composition, wt %		
	[kt], wt %	*T*, °C		*n* = 2	*n* = 3	*n* = 4, 5
Y	10	110	53.9	66.4	22.8	10.8
	20	90	39.8	64.1	25.8	10.1
	20	110	59.6	62.5	31.2	6.3
	20	120	68.2	63.3	27.6	8.1
	30	110	63.4	56.5	32.6	10.9
Beta	5	110	64.8	70.4	24.1	5.5
	10	110	93.7	72.1	24.4	3.5
	20	80	51.3	71.6	22.4	6.0
		100	91.6	72.3	23.1	4.6
		110	96.0	71.8	25.2	3.0
ZSM-12	5	110	45.7	85.2	11.8	3.0
	10	110	83.8	83.3	14.9	1.8
	20	80	41.4	81.7	15.3	3.0
		90	91.4	83.8	13.7	2.5
		110	98.3	83.2	14.7	2.1
		120	99.1	81.7	16.3	2.0
	30	110	99.5	81.6	16.3	2.1

To explain the results obtained, let us consider the acid properties of the zeolites as well as their structural characteristics. According to the data presented in Fig. 3 [20], the concentration of Brönsted acid sites (BAS) is maximal in the zeolite Y sample. The strength of the structural OH groups located in large cavities of the zeolite is 1170 kJ/mol on the PA scale. In addition, the acidic AlOH groups of two different types with strengths of 1189 and 1265 kJ/mol are present. The BAS concentration in the samples of zeolites Beta and ZSM-12 [21] is considerably lower than in zeolite Y; however, the strength of the acid sites is higher, 1165 kJ/mol. Note the high concentration of Lewis acid sites (LAS) in zeolite Beta, since it is known that they can transform into BAS in the reaction with water [23].

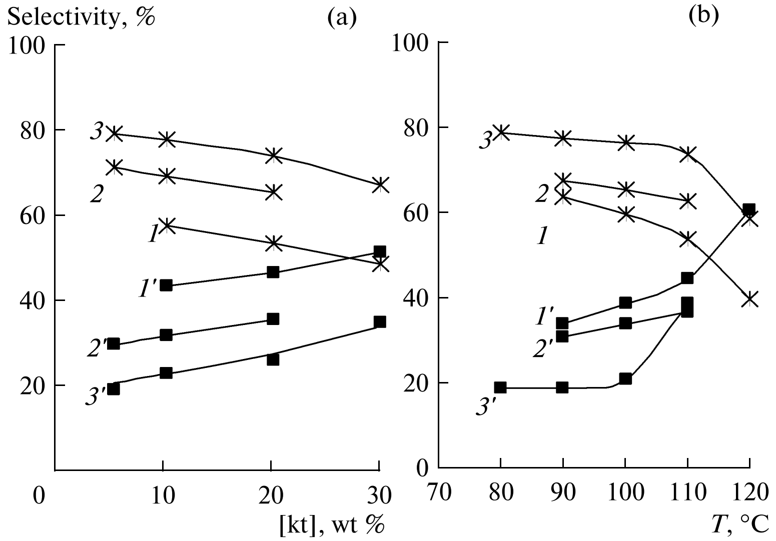

Fig. 2. Influence of (a) the catalyst concentration and (b) reaction temperature on the dimer formation selectivity in the presence of zeolites (*1*) Y, (*2*) Beta, and (*3*) ZSM-12; reaction conditions: (a) 110°C, 1 h; (b) 20 wt % of catalyst, 1 h. (*1*–*3*) Linear dimers and (*1'*–*3'*) cyclic dimers.

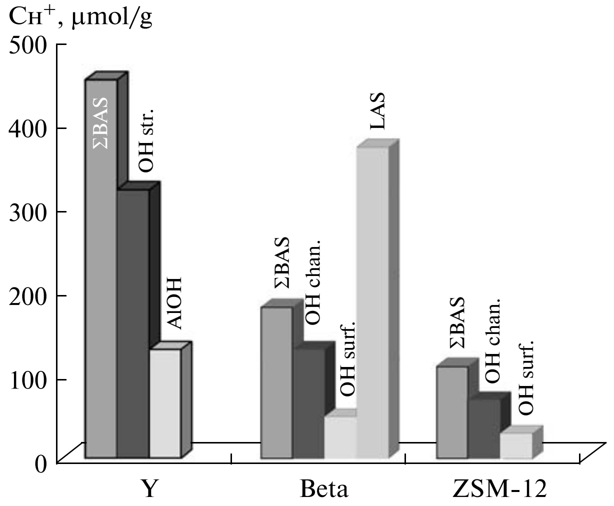

Fig. 3. Acid properties of zeolites Y, Beta, and ZSM-12. ΣBAS is the total concentration of Brönsted acid sites; LAS is the total concentration of Lewis acid sites; OH str. are structural OH groups in the cavities of zeolite Y; OH chan. are structural OH groups in the channels of the zeolites Beta and ZSM-12; OH surf. are surface acidic OH groups.

As the styrene dimerization proceeds via the cationic oligomerization mechanism, an increase in the Brönsted acidity of the catalyst must lead to an increase in its activity. Therefore, a maximal styrene conversion is expected in the presence of zeolites Y and Beta. Indeed, zeolite Beta displays a high activity in the reaction; however, a low styrene conversion is observed in the presence of zeolite Y. Probably, this is due to the crystal lattice structure of zeolite Y for which the diameter of the large cavity (1.2 nm) is more than that of the entrance window (0.8 nm) [24]. If the size of the molecules resulting from the oligomerization in the large cavity is more than the diameter of the entrance window, they remain in the cavity. Thus, the main part of BAS located in large cavities of zeolite Y is very quickly deactivated and the reaction is catalyzed by a small number of surface acid centers. As a consequence, the bulk oligomerization of styrene proceeds with a low monomer conversion and yields a large amount of high-molecular-mass oligomers.

When the oligomerization is carried out in a solvent, the styrene concentration in zeolite pores becomes lower, thereby reducing the possibility of the formation of large oligomer molecules ($n \geq 3$). In addition, the solvent accelerates the diffusion of the products from zeolite pores. As a result, the styrene conversion increases and the molecular-mass distribution of oligomers narrows.

For the reactions catalyzed by zeolites Beta and ZSM-12, the size of the resulting oligomers is limited by the diameter of the narrower straight channels (0.55 × 0.55 and 0.64 × 0.75 nm in zeolite Beta and 0.55 × 0.62 nm in zeolite ZSM-12) [24]. As a consequence, the reaction gives mostly linear styrene dimers (**Ia**, **Ib**).

It was found that both the activity and selectivity of zeolites in the styrene oligomerization are strongly dependent on the structure type of the zeolite. For the synthesis of the styrene linear dimers, the use of zeolite ZSM-12 is most favorable ($S = 82\%$, conversion 98–100 wt %). Zeolite Beta is close to zeolite ZSM-12 by activity and gives dimers as the main products (70–80%), mostly the linear isomer **Ia**. In the presence of the least active zeolite Y, styrene affords a complex mixture of oligomers in which dimers (53–60% in chlorobenzene) or dimers and trimers (60–80% in bulk) are predominant.

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