

## Cooligomerization of Styrene and $\alpha$ -Methylstyrene Catalyzed by $\gamma$ Zeolites

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### Abstract

It is ascertained that during the interaction of styrene and  $\alpha$ -methylstyrene in the presence of cation and cation-decated forms of zeolite Y the activity of zeolite catalysts increases in the following order: NiNaY  $\approx$  CaNaY < LaNaY  $\approx$  0,5HNaY < LaHY < NiHY  $\leq$  0,96HY. The product of reaction in the presence of cation forms of zeolite (NiNaY, CaNaY, LaNaY) is a mixture of low-molecular ( $n=2-4$ ) and high-molecular oligomers ( $n=14$ ). Oligomers with the degree of oligomerization 2 - 8 are formed in the presence of other zeolite samples. Zeolites 0,96HY and NiHY allow to receive gomo- and codimers with selectivity 68-80%. The main product of codimerization is cyclic dimer 1,1 - dimethyl - 3-phenylindane.

### Abbreviations

$\alpha$ -ms	$\alpha$ -methylstyrene
CD	cyclic dimer
LD	linear dimer
MWD	molecular-weight distribution
St	styrene

### Introduction

We showed in our previous works [1-3] that zeolites of type FAU (in particular, zeolite Y) give wide opportunity for regioselective realisation of both linear and cyclic gomodimerization vinylarenes. The effective methods of obtaining linear (1a, b) and cyclic (1c) dimers of  $\alpha$ -methylstyrene with selectivity above 90% and low-molecular oligomers of styrene (dimers 2a,b,c and trimers) with selectivity to 70-80% with the use of H-forms of zeolites Y, which have SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio = 5,5-6,0 and various degree of decationation have been developed.

Linear dimers of vinylarenes are used as regulators of molecular weight of polymers, plasticizers and also in the production of synthetic lubricant oils [4-8]. On the basis of cyclic dimers fuel and radiation-stable heat-transfers are obtained.

Also, they are used for producing monomers, applied for the synthesis of gas-separation membranes [9-10].

In our opinion, the cooligomers of styrene and  $\alpha$ -methylstyrene will have no less useful properties in comparison with dimers of vinylarenes.

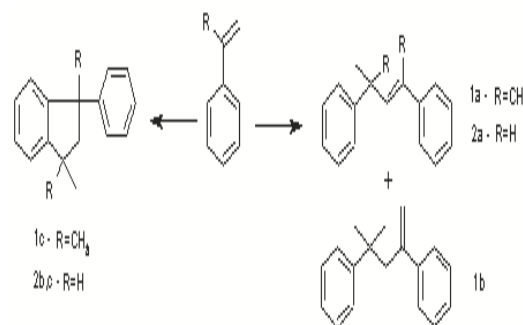


Fig. 1 Gomo-dimerization of styrene and  $\alpha$ -methylstyrene

Before starting our experiments there was not any information in the literature about the possibility of cooligomerization of styrene and  $\alpha$ -methylstyrene with the use of zeolites as a catalysts. Only obtaining a mixture of cyclic gomo- and

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codimers of styrene and  $\alpha$ -methylstyrene of codimerization of vinylarenes in the presence of phosphoric acid was described [11].

According to the above-mentioned information and also with the purpose of development of the perspective method of obtaining linear and cyclic cooligomers vinylarenes, we have studied the cooligomerization of styrene and  $\alpha$ -methylstyrene in the presence of zeolites of FAU (Y) type. The zeolites were used in the hydrogen and in cation-exchange form, as it is known that the introduction of metal-cation leads to changes of acid properties of zeolites and it influences on their activity and selectivity.

## Experimental

### Chemicals and materials

The samples of zeolite Y ( $\text{SiO}_2/\text{Al}_2\text{O}_3=6,0$ ) in the Na-form were synthesized by the methods described [12]. The samples NiNaY (content of Ni 6,1% wt.), CaNaY (5,4% wt. Ca) and LaNaY (8,8% wt. La) catalysts were prepared by ion exchanging of NaY zeolite once with aqueous solutions of the appropriate salts. After the exchange procedure, the loaded zeolites were filtered and rinsed with deionized water and dried in air at 540°C for 4 h. The protonic forms of the zeolites were prepared from the sodium form by ammonium exchange with  $\text{NH}_4\text{Cl}$  solution with various exchange degree  $\text{Na}^+$  on  $\text{H}^+$  ions – 50 % (0,5HNaY) and 96 % (0,96HY).

Zeolites NiHY (3,1% wt. Ni) and La-HY (9,6% wt. La) were prepared by an ion exchange of zeolite 0,96HY. The content of corresponding cations of zeolite samples (in recalculation on oxides) was determined using a Philips-PW 1480 X-ray fluorescence spectrometer (XRF). Before experiments on styrene and  $\alpha$ -methylstyrene cooligomerization the catalyst samples were heated in air for 4 h at 540°C.

Styrene manufactured by OAO "Salavatnefteorgsyntes" and  $\alpha$ -methylstyrene manufactured by OAO "Ufaorgsyntes" were distilled, before the experiments.

### Cooligomerization

The cooligomerization of styrene and  $\alpha$ -methylstyrene was carried out in periodical isothermal reactor at 80-120°C in the presence of

10-20 wt.% catalyst, in chlorobenzene and without a solvent. The reaction mass was separated from the catalyst by filtering after the reaction termination. The current concentration of vinylarenes and quantitative composition of dimeric fractions were determined by GLC-analysis. Composition of formed oligomers was determined by HPLC. The dimers and trimers were isolated by vacuum distillation for calibration.

The homo-dimers of styrene and  $\alpha$ -methylstyrene (1,2) were identified, using in advance synthesised compounds [1,13]. Chemical structure of linear (3-5) and cyclic codimers (6) were determined by NMR- and GH/HM – spectroscopy.

### Analysis

$^1\text{H}$  and  $^{13}\text{C}$  NMR-spectra were recorded on a «Bruker AVANCE – 400» spectrometer, ( $^1\text{H}$ , 400,13 MHz;  $^{13}\text{C}$ , 100,62 MHz) in  $\text{CDCl}_3$ . 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  $\text{min}^{-1}$ ; the electron impact (70 eV). GLC – analysis was carried out on the HRGS 5300 Mega Series chromatograph (Carlo Erba) with a flame-ionization detector (a capillary column 25 m, SE-30 phase, temperature-programmed heating from 50 to 280°C at a rate of 8°C  $\text{min}^{-1}$ , detector temperature 250°C, evaporator temperature 300°C, helium as a carrier gas, 30  $\text{ml min}^{-1}$ ). The analysis high-performance liquid chromatography (HPLC) was performed on a HP-1090 chromatograph with a refractometric detector and a Plgel 100Å polystyrene column using toluene as an eluent, a toluene flow rate of 0,8  $\text{mL min}^{-1}$  and a tape of velocity of 1,5  $\text{cm min}^{-1}$ .

### *trans*-3-Methyl-1,3-diphenylbut-1-ene (3) and 2,4-Diphenylpent-2-ene (4)

Zeolite NiHY (2,2 g) was added to the mixture of styrene (5,2 g, 5 mmol) and  $\alpha$ -methylstyrene (5,9 g, 0,05 mmol) in chlorobenzene (25ml) at 120°C and agitated at this temperature for 5 h. After cooling the catalyst was filtered from the reactionary mixture, then the solvent and not reacted vinylarenes, which did not react, were removed at the decreased pressure. Fractions of dimers (8,1 g) (120-135°C/2 mm hg) were isolated with distillation from the received mixture of

oligomers (dimers - 78,1%, trimers and higher molecules - 21,9%).

Cyclic dimers (1c; 2b,c; 6) (60%) were separated by means of crystallization from ethanol from fractions of dimers, then the received concentrate of linear gomo- and codimers vacuum was distilled.

The fraction with the maximum content of linear codimers (3 21,5 %; 4 28,3 %) was analyzed with the  $^1\text{H}$  and  $^{13}\text{C}$  NMR-methods.

We used methods one-dimensional ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and two-dimensional homo (COSY) and heteronuclear (HSQC, HMBC) spectroscopy to proof the structure of linear codimers 3, 4 (*trans*-3-methyl-1,3 - diphenylbut-1-ene, 2,4 - diphenylpent - 2-ene). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR-spectra contained groups of exceeding signals ( $\delta_{\text{H}}$ ): 6.95-7.43 (H, m, ArH) and 121.91-148.73 (s, Ar), correspondingly.

***trans*-3-Methyl-1,3-diphenylbut-1-ene (3)**  $\delta_{\text{H}}$ (400,13 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ ) 1,70 (6 H, s, 2 $\text{CH}_3$ ), 6,60-6,65 (2H, m, J, CH=CH), 7,0-7,6 (10H, m, ArH);  $\delta_{\text{C}}$  (100,62 MHz;  $\text{CDCl}_3$ ; ) 28,89 ( $\text{CH}_3$ ), 40,94 (CH), 126,09 (=CH), 140,30 (=CH); m/z: 222; Kovae index  $I_{\text{k}}$  1820.

**2,4-Diphenylpent-2-ene (4)**  $\delta_{\text{H}}$  (400,13 MHz;  $\text{CDCl}_3$ ; ) 1,60 (3H, d, J 7.0,  $\text{CH}_3$ ), 2,26 (3H, s,  $\text{CH}_3$ ), 4,03 (1H, m, CH), 6,11 (1H, d, = CH), (10H, m, ArH);  $\delta_{\text{C}}$  (100,62 MHz;  $\text{CDCl}_3$ ; ) 16,26 ( $\text{CH}_3$ ), 22,61 ( $\text{CH}_3$ ), 38,47 (CH), 133,59 (HC=), 143,83 (=C); m/z: 222 ( $\text{M}^+$ , %); Kovae index  $I_{\text{k}}$  1830.

**2,4-Diphenylpent-1-ene (5)** m/z: 222; Kovae index  $I_{\text{k}}$  1746.

#### 1,1-Dimethyl-3-phenylindane (6)

Zeolite 0,96HY (2,2 g) was added to the mixture of styrene (5,2 g, 5 mmol) and  $\alpha$ -methylstyrene (5,9 g, 5 mmol) in chlorbenzene(25  $\text{cm}^3$ ) at 130°C and agitated at this temperature for 5 h. After cooling the catalyst was filtered from the reactionary mixture, then the solvent was removed at the decreased pressure. Fractions of dimers (6,5 g) (120 - 135°C/2 mm hg) were isolated by means of distillation. The mixture of cyclic dimers was obtained by crystallization from hexane. The composition of these dimers is (wt.%): 6 - (48,7%); 1,1,3 - trimethyl-3-phenylindane (1c) - (48,2%); cyclic dimers styrene- (3,1%). The compound 6 was identified in the mixture by means of NMR-spectroscopy. The NMR-spectra  $^1\text{H}$  and  $^{13}\text{C}$  contained groups of exceeding signals (s,  $\delta_{\text{H}}$ ): 6.95-7.43 (H, m, Ar) and 121.91-148.73 (s, ArH), correspondingly.

**1,1-Dimethyl-3-phenylindane (6)**  $\delta_{\text{H}}$  (400,13 MHz;  $\text{CDCl}_3$ ; ) 1,36 (3H, s,  $\text{CH}_3$ ), 1,40 (3H, s,  $\text{CH}_3$ ), 1,79 (1H, m,  $\text{CH}_2$ ), 2.06 (1H, m,  $\text{CH}_2$ ), 4.43 (1H, tr,

CH);  $\delta_{\text{C}}$  (100,62 MHz;  $\text{CDCl}_3$ ; ) 29.70 ( $\text{CH}_3$ ), 29.10 ( $\text{CH}_3$ ), 46.64 ( $\text{C}(\text{CH}_3)_2$ ), 49.04 (CPh), 52.79 ( $\text{CH}_2$ ); m/z: 222; Kovae index  $I_{\text{k}}$  1713.

### The results and their discussion

We established earlier during the study of oligomerization of individual styrene and  $\alpha$ -methylstyrene in the presence of zeolite HY [1-3] that gomo-oligomerization of styrene proceeds at a higher temperature (90-110°C), than gomo-oligomerization of  $\alpha$ -methylstyrene (50-80°C). In case of oligomerization of styrene without any solvent the product of reaction is a mixture of low-molecular (degree of oligomerization n=2-6) and high-molecular compounds (n=14). In the solvent we can observe, in general, the formation of dimers and trimers of styrene in the structure of which linear isomers slightly prevail over cyclic ones. During the experiments with  $\alpha$ -methylstyrene linear dimers (1,3> 90 %) at 60-80°C or cyclic (4) at the temperature above 100°C are predominantly formed.

The results of cooligomerization of styrene and  $\alpha$ -methylstyrene in the presence of zeolites Y are shown in the tables 1,2. As it was expected, the conversion of styrene at 80°C (both during the reaction in a solvent and without it) is much lower, than the conversion of  $\alpha$ -methylstyrene. The speed of oligomerization of styrene increases with the rise of the temperature up to 120°C, and the degree of conversion of the both monomers becomes close (though, not in all cases).

It was found that zeolites NiNaY and CaNaY show the lowest catalytic activity in the cooligomerization of styrene and  $\alpha$ -methylstyrenes. The conversion of monomers in their presence during the reaction in a solvent is close to zero, and in the absence of any solvent it makes 8,0-21,5% for styrene and 5,2-10,2 % for  $\alpha$ -methylstyrene (Table 1). The zeolites LaNaY and 0,5HNaY possess close activity: in their presence the conversion of styrene makes 32,5-39,6 % (120°C, without any solvent) and 33,6-35,1 (in a solvent),  $\alpha$ -methylstyrene - 46,2-54,8 % (120°C, without any solvent) and 60,3-66,1% (in a solvent). The activity of zeolite LaHY is a little higher. As zeolites NiHY and 0,96HY are the most active in the reaction, the conversion of both monomers on them increases up to 77-98 wt.% during 1-3 h (the reaction in chlorbenzene). Hence, the activity of zeolite catalysts in the codimerization of styrene and  $\alpha$ -methylstyrene increases as the following: NiNaY  $\approx$  CaNaY <LaNaY  $\approx$  0,5HNaY <LaHY <NiHY  $\leq$  0,96HY.

**Table 1**

The composition of homo- and cooligomers, obtained by the cooligomerization of styrene and  $\alpha$ -methylstyrene without chlorobenzene (1-8) and in chlorobenzene (9-16) in the presence of zeolites Y

№	Catalyst	[M] <sub>0</sub> , mol/l	Catalyst loading, wt%	T, °C	Conversion (%)		Selectivity (%)				
					St	$\alpha$ -ms	n=2	n=3	n=4	n=5-8	n=14
1	0,5HNaY <sub>6,0</sub>	-	20	120	60,5	75,1	43,8	25,8	13,2	17,2	-
2	0,96HY <sub>6,0</sub>	-	20	80	57,3	92,6	41,9	15,7	12,0	30,4	-
3		-	20	120	93,5	98,5	43,8	19,9	12,6	23,6	-
4	LaNaY	-	10	120	32,5	46,2	20,5	-	-	18,7	60,8
5	LaHY	-	10	120	70,6	86,2	28,2	22,6	17,5	31,7	-
6	NiNaY	-	10	120	8	10,2	16,2	3,0	0,6		80,2
7	NiHY	-	10	120	67,4	90,4	49,5	18,9	12,8	18,8	
8	NaCaY	-	20	120	30,8	5,2	4,4	-	-	14,5	81,1
9	0,5HNaY <sub>6,0</sub>	4	10	120	35,1	66,1	61,7	14,6	7,2	16,5	-
10	0,96HY <sub>6,0</sub>	4	20	80	76,2	96,4	63,0	21,8	7,2	8,0	-
11		4	10	120	84,0	99,7	62,6	18,7	9,6	9,1	-
12		2	10	120	99,5	100,0	67,9	21,6	5,4	5,1	-
13		4	20	120	100,0	100,0	63,1	21,7	6,9	8,3	-
14	LaNaY	4	10	120	33,6	60,3	65,4	16,0	10,3	3,3	5,0
15	LaHY	4	10	120	54,2	73,4	46,3	25,3	12,1	16,3	-
16	NiHY	2	10	120	100,0	100,0	79,1	13,5	5,7	1,7 <sup>a</sup>	-

<sup>a</sup> - n = 5,6, <sup>b</sup> mol a ratio of styrene: $\alpha$ -methylstyrene = 1:1, <sup>c</sup> reaction time = 5 h

The findings about the activity of zeolites, which were studied, are in general close to those ones concerning acid properties of zeolites NaY and HY after ion exchanging, which were described in the literature. The proton centers are practically absent for zeolite NaY after the exchange for Ca<sup>2+</sup> and Ni<sup>2+</sup> in the quantity less than 80 %. At the same time in work [14] was showed that stronger proton centers (PA = 1180 kJ/mol) appear with the introduction of trivalent cations, for example La. The introduction of cations of two – (Ba<sup>2+</sup>, Ca<sup>2+</sup>) and trivalent metals (La<sup>3+</sup>) in zeolite HY, as it is shown in the works of the Japanese authors [15,16] leads to the reduction of concentration of acid OH-groups, localized in hexagonal prisms, in the sodalite cages as well as in the super cages. At that the strength of the Brønsted acid sites increases, because of polarizing and inductive effects of introduced metal cation. The high activity of zeolite NiHY is apparently determined, by the fact that

cations Ni<sup>2+</sup> form active sites of oligomerization of olefins [17].

The nature of the exchange cation, as it can be seen in Tables 1 and 2, influence essentially on the degree of oligomerization of the products of codimerization of styrene and  $\alpha$ -methylstyrene. We should note that we cite the results of cooligomerization of styrene and  $\alpha$ -methylstyrene, received at the equal mol ratio of vinylarenes (1:1). Prediscovery of the influence of mole ratio of the vinylarenes on the structure of oligomers has shown that the increase of the part of  $\alpha$ -methylstyrene promotes to decrease yield of oligomers with n>3. At a ratio of styrene:  $\alpha$ -methylstyrene = 1:5 the yield of dimers amounts 74%, however the total yield of codimers decreases. The surplus of styrene in the mixture of monomers leads to widening of the molecular-weight distribution (MWD) of oligomers and to considerable decrease in the yield of dimers.

The oligomers, obtained at the presence of cation forms of zeolite Y (NiNaY, CaNaY and LaNaY) represent a mixture of low-molecular (degree of oligomerization  $n = 2-4$ ) and high-molecular-weight hydrocarbons ( $n = 14$ ). The detailed structure of dimers will be discussed later; we will only mention that, in the specified group of compounds, along with the codimers of styrene and  $\alpha$ -methylstyrene, there are also their homo-dimers. In the structure of trimers, according to the data of the GH/HM – spectroscopy, there are 80-95% cooligomers from m.w. 326 (formed as the result of interaction of 2 molecules of styrene and 1 molecule of  $\alpha$ -methylstyrene) and m.w. 340 (the products of interaction of 1 molecule of styrene and 2 molecules  $\alpha$ -methylstyrene), 5-15 % trimers of styrene and up to 3 % trimers of  $\alpha$ -methylstyrene. The preliminary experiments on studying the transformations of individual styrene and  $\alpha$ -methylstyrene in the absence of the catalyst at 80-120°C have shown that unlike  $\alpha$ -methylstyrene which in these conditions is slightly oxidized to acetophenon and phenylpropionic aldehyde, oligomers with degree of oligomerization close to 14 are formed. That is why the high-molecular-weight fraction which can be observed during the cooligomerization of styrene and  $\alpha$ -methylstyrene on zeolites NiNaY, CaNaY and LaNaY, we should apparently refer to the products of thermal oligomerization of styrene.

High-molecular-weight oligomers are not formed on high-decationated sample 0,96HY, as well as on the cation-exchanged zeolites 0,5HNaY, LaHY and NiHY. The degree of oligomerization of the compounds obtained in the presence of zeolites 0,5HNaY, 0,96HY, LaHY makes 2-8. Oligomers, obtained in the presence of zeolite NiHY, have

narrower MWD, their degree of oligomerization is equal to 2-6.

Unlike zeolite LaHY in the presence of which vinylarenes interact with the predominant formation of oligomers with the degree of oligomerization  $\geq 3$ , on zeolites 0,5HNaY, 0,96HY and NiHY oligomers are formed with the prevalence of dimers (60-79 %).

The composition of oligomers can be regulated by carrying out the reaction in a solvent or without it. The products with higher yield of dimers and the less quantity of oligomers with  $n = 4-8$  were received in chlorbenzene.

On the example of zeolites 0,96HY and NiHY we show that the decrease of initial concentration of monomers in a solvent  $[M_0]$  from 4 mol/l to 2 mol/l allows to increase the yield of dimers from 62 to 68 wt.% on zeolite 0,96HY and from 69 to 79 wt.% on zeolite NiHY. The quantity of oligomers with the degree of oligomerization  $n \geq 4$  thus decreases in two times.

The research of the composition of dimers has shown that during the interaction of styrene and  $\alpha$ -methylstyrene the formation of gomodimers of styrene (2a - 1,3-diphenyl-but-1-ene; 2b and 2c - *cis*- and a *trans*-1-methyl-3-phenylindane) and  $\alpha$ -methylstyrene (1a,b - 4-methyl-2,4-diphenylpentene-1; 4-methyl-2,4-diphenylpentene-2; 1c - 1,1,3-trimethyl-3-phenylindane) cannot be avoided.

As a result of identification of chemical structure of codimers (3-6), the scheme of codimerization of styrene and  $\alpha$ -methylstyrene in the presence of zeolites Y can be presented as the following:

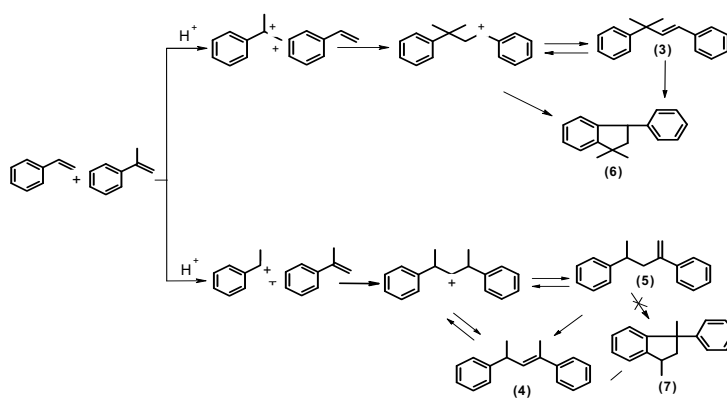


Fig. 2. Formation of codimers of styrene and  $\alpha$ -methylstyrene

**Table 2**  
The composition of homo- and cooligomers, obtained by the cooligomerization of styrene and  $\alpha$ -methylstyrene without chlorobenzene (1-6) and in chlorobenzene (7-11) in the presence of zeolites Y

№	Catalyst	Catalyst loading, wt%	T, °C	[M] <sub>0</sub> , mol/l	Reaction time, h	Codimers			Dimers of styrene, %			Dimers of $\alpha$ -methylstyrene, %		
						$\Sigma$	CD	LD	$\Sigma$	CD	LD	$\Sigma$	CD	LD
1	0,5HNaY <sub>6,0</sub>	20	120	-	5	24,2	20,1	4,1	4,2	2,6	1,6	71,6	9,6	62,0
2	0,96HY <sub>6,0</sub>	20	80	-	5	17,8	14,5	3,4	2,9	1,1	1,7	79,3	6,3	73,0
3		10	120	-	5	39,4	32,6	6,8	8,4	4,7	3,7	51,6	18	33,6
4		20	120	-	5	54,2	44,5	9,7	7,4	3,3	4,1	38,4	25,7	12,7
5	NiHY	10	120	-	5	37,6	24,5	13,1	18,6	8,7	10,0	43,8	10,9	32,9
6	LaHY	10	120	-	5	38,7	24,4	14,3	10,8	3,9	6,9	50,5	10,0	40,5
7	0,5HNaY <sub>6,0</sub>	10	120	4	5	22,9	19,6	3,3	2,6	1,7	0,9	74,5	11,4	63,1
8	0,96HY <sub>6,0</sub>	20	80	4	5	36,7	29,4	7,3	11,1	6,2	4,9	52,2	16,7	23,4
9		10	120	4	5	41,3	33,2	8,1	16,6	8,0	8,6	42,1	11,7	30,4
10		20	120	2	5	48,6	39,1	9,5	13,7	7,7	6,0	37,7	37,7	-
11	NiHY	10	120	4	3	53,6	33,1	20,5	15,2	1,0	14,2	31,2	10,9	20,3

<sup>a</sup>mol ratio styrene:  $\alpha$ -methylstyrene = 1:1

The change of the composition of dimers, obtained on the samples of zeolite HY with various degree of decationation 0,5HNaY and 0,96HY, and also on zeolite NiHY, depending on the conditions of the reaction are shown in Table 2.

It is possible to mention that during the interaction of styrene and  $\alpha$ -methylstyrene in the absence of a solvent at 80°C on zeolites 0,5HNaY and 0,96HY we mainly obtained linear dimers of  $\alpha$ -methylstyrene (73,0-76,6 % wt. compounds 1a); and the number of codimers, formed in these experiments is about 18 wt.%. The ratio cyclic (CD) and linear (LD) dimers make 0,3:1. The rise of temperature to 120°C promotes to the increase of quantity of codimers (in 2-3 times) and of dimers styrene (in 2-2,5 times). The acceleration of reaction of intramolecular alkylation, which takes place with the rise of temperature, leads to increase of yield of cyclic isomers and ratio CD:LD changes in case of zeolite 0,5HNaY to 0,5:1, and in case of zeolite 0,96HY to 2,8:1.

Similarly, the cooligomerization of styrene and  $\alpha$ -methylstyrene in chlorbenzene on zeolite 0,5HNaY at 80°C proceeds with the formation of mainly linear dimers  $\alpha$ -methylstyrene (81,7 %); with the rise of temperature to 120°C in the composition of dimers the part of codimers and cyclic dimers of styrene and  $\alpha$ -methylstyrene increases (Table 2).

Close results on the composition of dimers have been received during the cooligomerization of styrene and  $\alpha$ -methylstyrene in chlorbenzene on zeolites 0,96HY and NiHY: the main products at 120°C are codimers (41,3-53,6 %) and dimers  $\alpha$ -methylstyrene (31,2-51,1 %), the quantity of dimers of styrene makes (2,7-16,6%).

We should note, that on all the studied samples of zeolites, except NiHY, in the composition of codimers ~80-90 % fall up to the part of the cyclic codimer (6). Codimers, received in the presence of zeolite NiHY, are characterized by higher percentage of linear codimers (3,4). The quantity of the codimer (3) does not exceed 30 % from the amount of linear dimers and decreases with the increase of temperature, the concentration of the catalyst and the time of the reaction as a result of transformation into cyclic codimer (6) (Figure 2). Insignificant (less than 1%) concentration of the compound (5) is obviously caused by quickly proceeding isomerization of this isomer into the codimer with internal double bond (4). It was expected that both of the codimers (4) and (5), formed on a route, will turn into corresponding

cyclic dimer- 1,3-dimethyl-3-phenylindan (7). However the indicated compound in the composition of dimers has not been revealed.

## Conclusions

Thus, the activity of studied in the cooligomerization styrene and  $\alpha$ -methylstyrene zeolites increases in the order: NiNaY  $\approx$  CaNaY < LaNaY  $\approx$  0,5HNaY < LaHY < NiHY  $\leq$  0,96HY. On the cation-exchanged zeolite forms (NiNaY, CaNaY, LaNaY) a mixture of low-molecular (n=2-4) and high-molecular oligomers (n=14) is formed. In the presence of other samples oligomers with the degree of oligomerization 2-8 have been obtained. Carrying out of the reaction in a solvent promotes to the yield increase of dimers, the selectivity of formation of which in the presence of zeolite NiHY reaches 79,3 %. The maximum quantity of codimers in dimer fraction (to 54 %) has been obtained during the cooligomerization of styrene and  $\alpha$ -methylstyrene on zeolites 0,96HY and NiHY. The main product of codimerization is cyclic dimer 1,1-dimethyl-3-phenylindane, formed as a result of interaction of carb-cation of  $\alpha$ -methylstyrene with a molecule of styrene.

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