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Dimerization of α-Methylstyrene on High-Silica Zeolites

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Abstract—α-Methylstyrene dimerization was studied on high-silica β, ZSM-12, and TsVN zeolites. The acid properties of the zeolites were studied by IR spectroscopy. It was revealed that the catalytic properties of the zeolites in α-methylstyrene dimerization depend on both the acidic and structural characteristics of the catalysts. The highest activity in the reaction was exhibited by zeolite β, as the maximum amount of acid sites were found in its structural units (inside channels, on the outer surface). Zeolite ZSM-12 had the highest selectivity for linear dimers.

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INTRODUCTION

The linear dimers of α-methylstyrene (4-methyl-2,4-diphenylpent-1- and 2-enes) and their hydrogenated derivatives hold promise as synthetic lubricating oils and radiation-resistant and insulating materials [1–3].

α-Methylstyrene dimers can be successfully synthesized in the presence of type Y zeolites, on which the selectivity for linear dimers is 90–92% at a feedstock conversion of 95–100% [4, 5].

It is known that high-silica zeolites differ from zeolites Y in structure, as well as in the concentration and strength of acid sites; therefore, it was of interest to study the dimerization of α-methylstyrene in the presence of high-silica zeolites β, ZSM-12, and TsVN. The obtained data on the catalytic properties of the zeolite catalysts were correlated with their acid characteristics, which were determined by IR spectroscopy.

EXPERIMENTAL

The H-forms of β (SiO_2/Al_2O_3 = 18), ZSM-12 (SiO_2/Al_2O_3 = 34) and TsVN (SiO_2/Al_2O_3 = 28.4) zeolite specimens were investigated in this work. The zeolites were synthesized at the Angarsk Catalyst and Organic Synthesis Plant (Russia).

The sample of β zeolite available in the NH_4 form was converted into the H form by calcination at 540°C.

Prior to experiments on α-methylstyrene dimerization, all catalyst samples were calcined in air at 540°C for 4 h.

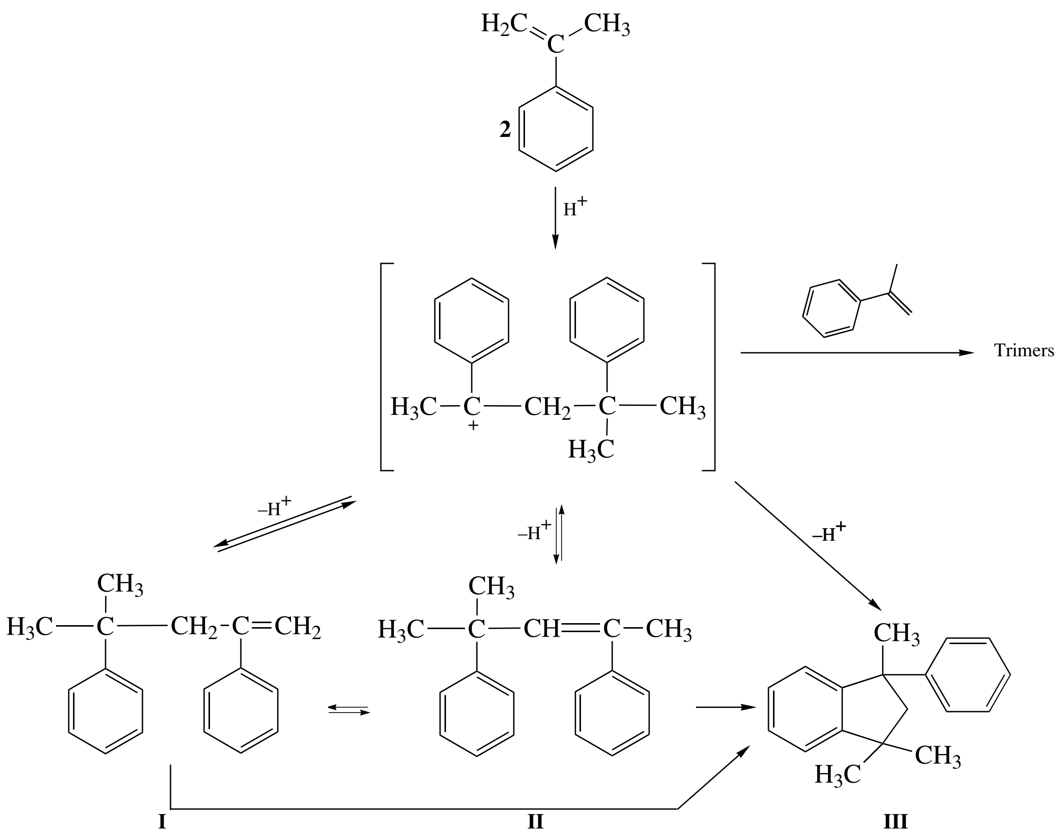
The catalytic properties of the zeolites in α-methylstyrene dimerization were studied in an isothermal batch reactor at 20–120°C and atmospheric pressure in the presence of 0.1–50.0 wt % zeolite catalysts. The reactant α-methylstyrene was distilled before the experiments; its purity was 99.8 wt %. The activity of the catalysts was measured as the conversion (K) of α-methylstyrene, and the selectivity for products was calculated by the formula $S_i = c_i/K$.

The synthesized hydrocarbons were analyzed on a Tsvet chromatograph equipped with a flame-ionization detector, a 2 m × 2 mm metal column packed with 5% SE-30-coated Chromaton HMDS, in the mode of temperature programming from 50 to 280°C at a rate of 8 K/min, and detectors and evaporator temperatures of 250 and 300°C, respectively, using helium as a carrier gas at a flow rate of 30 ml/min.

The acid properties of the zeolite specimens were studied by IR spectroscopy of adsorbed CO [6]. The IR spectra were recorded on a Shimadzu 8300 Fourier-transform spectrometer with a resolution of 4 cm^{-1} and a number of spectra accumulation equal to 50. The investigation procedure was described earlier [4].

RESULTS AND DISCUSSION

The dimerization of α-methylstyrene on zeolites yields dimers **I–III** and trimers:



The results of α-methylstyrene dimerization in the presence of the test zeolites are given in Table 1 and Figs. 1–3. It is seen that the main products are dimers of α-methylstyrene; the amount of trimers does not exceed 15%. The linear isomers dominate the dimer fraction under the given conditions.

It was found that TsVN zeolite exhibits the lowest catalytic activity in the reaction (Fig. 1). The conversion of α-methylstyrene on this catalyst increases proportionally to the amount of the catalyst. An increase in temperature slightly influences the conversion. These findings allow us to suppose that the reaction proceeds on the outer surface of zeolite crystals, not inside the channels.

The highest activity was exhibited by zeolite β; the dimerization of α-methylstyrene on this zeolite proceeds even at 20°C at an α-methylstyrene conversion higher than 95 wt %.

Table 1. α-Methylstyrene dimerization on zeolite catalysts

Catalyst	Reaction conditions			α-MS conversion, wt %	Selectivity, %			linear dimer/cyclic dimer
	[cat], wt %	*T*, °C	τ, h		linear dimer	cyclic dimer	trimers	
β	1	60	2.5	98.1	89.2	2.9	7.9	30.8
	2	20	4	94.3	86.0	3.4	10.6	25.3
	5	20	3	95.0	82.6	3.9	13.6	21.2
	10	20	0.5	95.1	81.9	4.7	13.4	17.4
ZSM–12	1	80	4	91.0	94.1	3.6	2.3	26.1
	5	40	3	24.6	94.6	2.0	3.4	47.3
	5	80	3	98.2	92.9	4.0	3.1	23.2
	0.5	60	6	94.4	93.7	3.3	3.0	28.4
TsVN	5	80	3	5.1	88.1	7.1	4.8	12.4
	50	80	3	77.8	78.6	6.6	14.8	11.9
	10	120	6	32.5	87.2	7.1	5.7	12.3

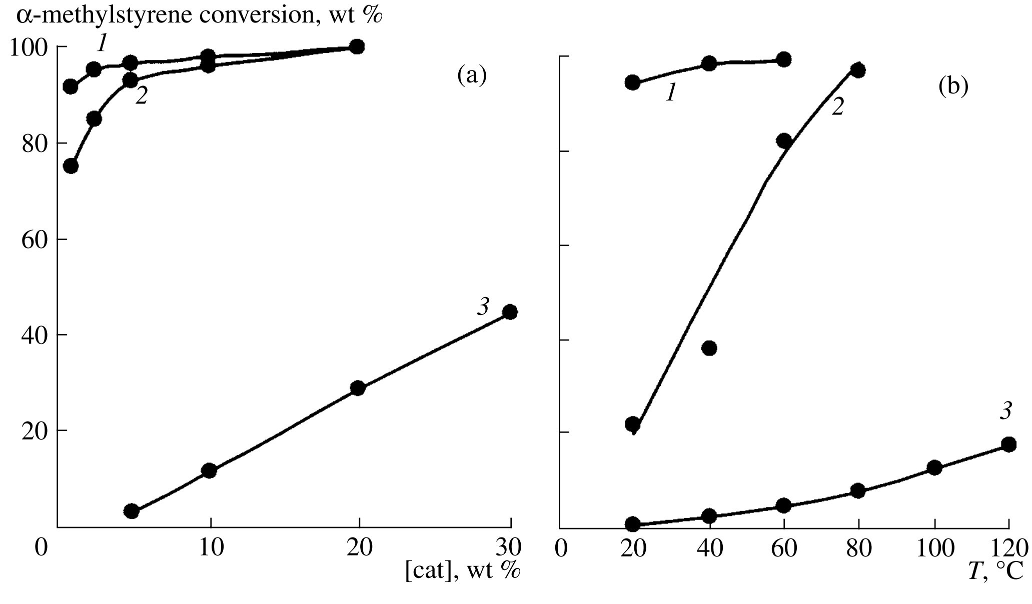


Fig. 1. Dependence of α-methylstyrene conversion over zeolites (*1*) β, (*2*) ZSM-12, and (*3*) TsVN on (a) the catalyst concentration and (b) temperature; reaction conditions: (a) $T = 80°C$; $\tau = 1$ h; (b) the amount of catalyst is 10 wt %, $\tau = 1$ h.

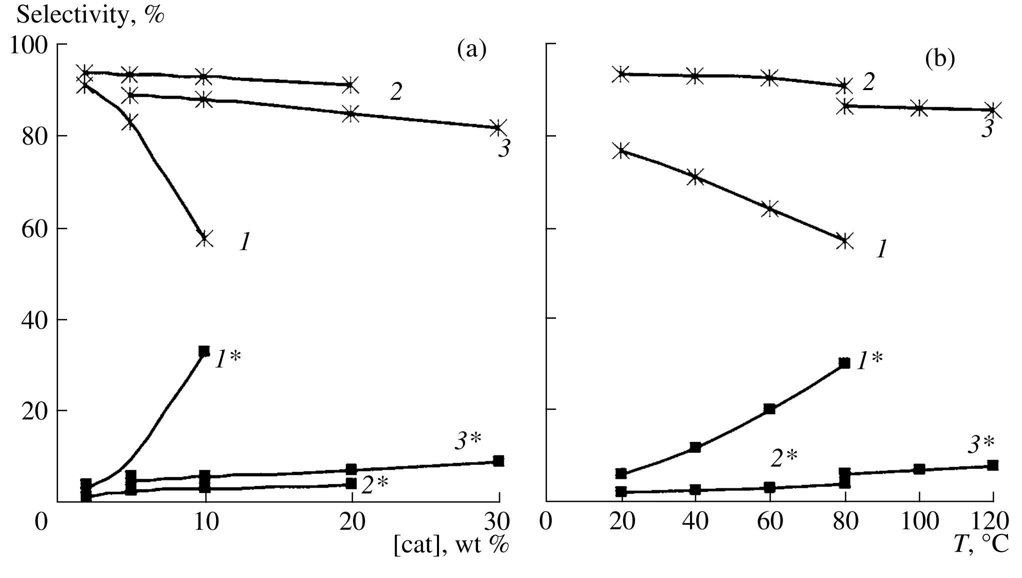


Fig. 2. Influence of the (a) catalyst concentration and (b) temperature on the selectivity for α-methylstyrene dimers: (*1*) β, (*2*) ZSM-12, and (*3*) TsVN; (*1–3*) selectivity for linear dimers; (*1*–3**) selectivity for cyclic dimer; reaction conditions: (a) $T = 80°C$, $\tau = 1$ h; (b) the amount of catalyst is 10 wt %, $\tau = 1$ h.

The conversion of α-methylstyrene on zeolite ZSM-12 is determined to a great extent by the reaction temperature: the conversion is negligible (20–30 wt %) at 20°C and reaches 100 wt % as the temperature increases to 60–80°C.

From Fig. 2, it is seen that the product selectivity depends on the type of zeolite and reaction conditions. A decrease in the selectivity for linear dimers with an increase in temperature or catalyst concentration is a common feature for all test catalysts. Zeolite ZSM-12 exhibits the highest selectivity for linear dimers: the selectivity S_{ld} is 90–94% at an α-methylstyrene conversion of 95–100 wt %, and the yields of the cyclic dimer and trimers are minimal (2–6 and 2–4%, respectively). The selectivity on TsVN zeolite is close to that on ZSM-12.

It was found that the selective synthesis of linear dimers (85–90%) on zeolite β is possible only at low temperatures (20–40°C) and catalyst concentrations up to 5 wt %. An increase in temperature, as well as in the catalyst concentration, results in a sharp decrease in the selectivity for linear dimers and increases the yield of the cyclic dimer. Figure 3, which shows a change in the ratio of linear to cyclic dimers in the catalyzates obtained at 80°C in the presence of 10 wt % catalyst, clearly demonstrates that the rate of cyclic dimer formation on zeolite β is much higher than that on ZSM-12.

The IR data on the acid properties of β, ZSM-12, and TsVN zeolite specimens are given in Table 2.

The spectra of OH groups of the test zeolites display absorption bands at 3615 cm^{-1} (due to vibrations of bridging Al–OH–Si groups in channels), 3738–3745 cm^{-1} (correspond to vibrations of bridging OH groups on the outer surface of crystals and weakly acidic terminal SiOH groups), 3670–3700 cm^{-1} (due to AlOH groups of extra-framework aluminum). In addition, the IR spectrum of zeolite β shows absorption bands at 3780–3790 cm^{-1} due to the vibrations of terminal AlOH groups.

As follows from the intensity of the absorption band at 3745 cm^{-1}, the maximum amount of OH groups corresponding to this band is present in zeolite β and the minimum amount is in zeolite TsVN.

During adsorption on the surface of a zeolite sample, carbon monoxide reacts with OH groups, forming H-bonded complexes. In this case, the OH absorption bands are shifted to lower frequencies. For all specimens, there are three bands relevant to hydrogen-bonded OH groups: at 3278 cm^{-1} (vibrations of bridging OH groups in channels), 3430 cm^{-1} (bridging OH groups on the outer surface), and 3640 cm^{-1} (SiOH groups).

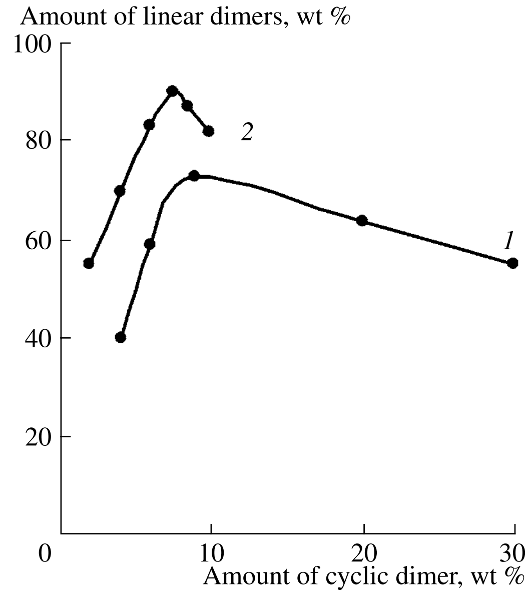


Fig. 3. Change in the concentration of α-methylstyrene dimers in the reaction mixture: (*1*) β, (*2*) ZSM-12; reaction conditions: *T* = 80°C, the amount of catalyst is 10 wt %.

From the data presented in Table 2, it follows that the highest concentration of Bronsted acid sites (BAS) is on β zeolite, and the strength of acid sites on all zeolites is the same.

At low temperatures, Lewis acid sites (LAS) also form complexes with CO, which give rise to IR absorption bands at 2186–2230 cm^{-1}.

The maximum amount of LASs (in terms of both type and concentration) was found for the zeolite β specimen. The IR spectrum of this sample exhibits a set

Table 2. Acid properties of zeolite catalysts

Specimen	Site type					
	LAS			BAS		
	ν_{CO}, cm^{-1}	N_{CO}, µmol/g	Q_{CO},* kJ/mol	ν_{CO}, cm^{-1}	N_H,** µmol/g	PA, kJ/mol
β	2232	12.3	55.0	2175	128	1165
	2224	43.0	51.0	2166	51	1165
	2214–2206	22.0	46–42.0			
	2197	49.0	37.5			
	2193	244.0	35.5			
ZSM–12	2228	4.0	53.0	2174	75	1165
	2215	0.9	46.5	2162	31	1165
	2189	1.1	33.5			
TsVN	2186	4.2	32.0	2174	104	1165
				2164	31	1165

* $Q_{CO} = 10.5 + 0.5 (\nu_{CO}\ 2143)$ [6].

** N_H is the concentration averaged over the CO and OH band (initial and after CO adsorption).

of 5 bands characteristic of zeolites: at 2193 cm^{-1} (CO complexes adsorbed on the alumina phase), 2200 cm^{-1} (nuclei of the alumina phase), 2215 cm^{-1} (BAS-localized nuclei of the alumina phase), 2223 cm^{-1} (presumably, tetrameric oxide–hydroxide aluminum clusters), and 2228–2232 cm^{-1} (BAS-bonded dimeric oxide clusters of aluminum).

The total LAS concentration on the zeolite β specimen was 370.3 μmol/g. About 80% of this amount falls to the share of CO complexes with nuclei of the alumina phase. The strength of these LASs as determined in terms of the heat of adsorption, Q_{CO}, is low (35.5–37.5 kJ/mol). The concentration of the strongest Lewis acid sites (Q_{CO} = 51.0–55.0 kJ/mol) is considerably higher than that on other specimens.

The IR spectrum of the zeolite ZSM-12 specimen exhibits the same absorption bands as in the case of zeolite β, although their intensity is considerably lower and an additional band appears at 2173 cm^{-1}. Correspondingly, the LAS concentration in this zeolite was 62 times lower.

The spectrum of zeolite TsVN sharply differs from that of the aforementioned two specimens and exhibits only one absorption band at 2186 cm^{-1}. The concentration and strength of Lewis acid sites on this specimen was minimal.

A comparison of the acidic and catalytic properties of the test zeolites shows that the zeolites can be arranged in the following order in terms of concentration of acid sites (both BAS concentration and the total concentration of acid sites): β > TsVN > ZSM-12. The activity of the catalysts in α-methylstyrene dimerization decreases in the order β > ZSM-12 $\gg$ TsVN.

Since the strength of Bronsted acid sites is the same (~1165 kJ/mol) in all test zeolites, the obtained dependence of the catalyst activity may mean that either not all acid sites of zeolite TsVN are accessible to α-methylstyrene molecules or the formed products cannot be desorbed onto the outer zeolite surface and, thus, block the zeolite channels that contain the main amount of acid OH groups inside. Zeolite TsVN has a porous structure similar to that of zeolite ZSM-5, i.e., a system of channels of two types: straight channels with a round 10-membered ring 0.56 nm in diameter and sinusoidal (elliptic) channels with a pore opening diameter of 0.51 × 0.55 nm. Obviously, it is difficult for α-methylstyrene molecules, which have dimensions of 0.43 × 0.72 nm, to penetrate inside zeolite channels, and is particularly impossible for α-methylstyrene dimers to diffuse inside the channels. Owing to these constraints, the transformation of α-methylstyrene proceeds on active sites located on the outer zeolite surface (about 30% of total amount of OH groups).

The high activity of zeolite β seems to be determined by several factors. First, as has been mentioned above, zeolite β has a high concentration of Lewis sites (twice that of Bronsted sites). Their presence in the zeolite was detected after calcination of the specimen at 450°C under high-vacuum conditions. Under low-temperature (<100°C) α-methylstyrene dimerization conditions at atmospheric pressure, Lewis acid sites can react with water molecules to form a Bronsted site unless special measures are taken (e.g., sealing) to prevent the contact of the reaction mixture with the environment. Thus, it is likely that zeolite β in actuality contains a much greater number of Bronsted sites AC than was determined by IR spectroscopy. Second, according to [6], Lewis sites in high-silica zeolites are situated in places of connection of microcrystals, i.e., on the outer zeolite surface, and, hence, are the most accessible to reacting molecules. The great amount of easily accessible acid sites can ensure the effect of high activity of this catalyst. Note that the role of these acid sites undoubtedly increases with a rise in the reaction temperature and that they make the main contribution to the reactions of intramolecular alkylation and cyclization leading to the formation of the cyclic dimer.

The different selectivities for linear and cyclic dimers on ZSM-12 and β-zeolites are associated with the peculiarities of the acid properties of the catalysts, as well as with their porous structure. Taking into account the obtained data on acidity, this difference may be explained by the fact that the amount of OH-groups on the outer surface of β-zeolite is 1.7 times that on ZSM-12. Therefore, conditions for the formation of bulkier molecules of cyclic dimer and trimers are favorable on zeolite β.

The appearance of a molecular-sieving effect of zeolites also cannot be excluded. It is known [7] that the porous structure of zeolite β represents a three-dimensional system of two-type straight channels connected with each other and formed by 12-membered rings with mouth dimensions of 0.55 × 0.55 nm and 0.64 × 0.75 nm. In zeolite ZSM-12, straight channels are also formed by 12-member rings with a mouth size of 0.55 × 0.62 nm. Apparently, the cyclic dimer of α-methylstyrene more readily forms and diffuses from wide straight channels of zeolite β than from the narrower channels of ZSM-12. However, the pore size of zeolite ZSM-12 is optimal for the formation and diffusion of linear dimers.

CONCLUSIONS

It was found that the catalytic properties of zeolites β, ZSM-12, and TsVN in α-methylstyrene dimerization are determined by differences in concentration and strength of acid sites, as well as by the molecular-sieve properties of the catalysts (channel size, location of acid sites inside the channels or on the outer surface of crystals).

Zeolite β exhibits the highest catalytic activity in the reaction, as it possesses the maximum total concentration of Bronsted and Lewis acid sites occurring in wide channels (BAS) and on the outer surface of crystals (LAS).

Zeolite ZSM-12 is the most selective for linear dimers of α-methylstyrene, since the formation and diffusion of cyclic dimer is difficult in its channels.

The low conversion of α-methylstyrene on zeolite TsVN is due to the fact that acid sites occurring in narrow channels are inaccessible to α-methylstyrene molecules.

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