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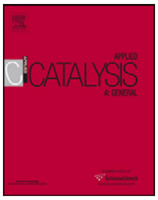

Codimerisation of styrene and α-methylstyrene in the presence of zeolites

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ABSTRACT

The reaction of styrene with α-methylstyrene has been studied over Y, Beta and ZSM-12 zeolites at 80–120 °C in the presence or absence of chlorobenzene. Homo- and codimers of styrene and α-methylstyrene were the main reaction products. The yield of dimers and their structure depends on zeolite type and the experimental conditions. Dimers were formed with greater selectively over zeolite HZSM-12 ($S = 80–83\%$), for which the structural features promote the synthesis of linear compounds. In the presence of the zeolites HY and HBeta, cyclic homo- and codimers were the predominant products. The yield of dimers increases with increased reaction temperature and catalyst concentration, and in the presence of solvent. All zeolites investigated showed high codimerisation activity on styrene and α-methylstyrene at 120 °C.

1. Introduction

Linear dimers of α-methylstyrene are used as polymer and rubber molecular-weight regulators and plasticisers, and employed in dielectric liquids and solvents [1–4]. High-performance lubricating materials are manufactured from hydrogenated dimers [2]. Fuel and radiation-resistant heat-transfers fluids and monomers, used in the synthesis of gas-separation membranes, are produced from cyclic dimer of α-methylstyrene [5,6]. Styrene dimers are promising as components of epoxide resins, varnishes, paints, and polyvinylchloride materials [7–10].

The catalytic homodimerisation of styrene and α-methylstyrene proceeds, depending on the nature of the catalyst and the reaction conditions, to form dimers with linear **(1a; 1b, 2a)** or cyclic **(1c; 2b,c)** structures (Scheme 1) [11,12].

Large pore zeolites and zeolite-like materials have been shown to exhibit high efficiency in the homodimerisation of vinylarenes [13–22].

These zeolites contain 12-ring or 14-ring Si–O–Al–, which form entrance windows into the channels or cavities of zeolites. Wide pores provide access for reagent molecules to acidic catalytic sites and allow transport of the reaction products from zeolite channels.

The regioselectivity of the formation of preferentially linear dimers or cyclic dimers depends on both structure of zeolite and its acidic characteristics. The linear dimer of styrene-1,3-diphenylbut-1-ene was synthesised with a selectivity of 81% in the presence of Y zeolites with a degree of proton exchange of 10% (55 wt.% of the catalyst, concentration of styrene in CH_2Cl_2, 0,2 mol l^{-1}, 25 °C) [13]. The cyclic dimers of styrene-*cis*- and *trans*-1-methyl-3-phenylindane 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^{-1}) [14]. The zeolite-like crystalline aluminophosphates $AlPO_4$-8 exhibited a high activity in dimerisation of α-methylstyrene [15]. The transformation is characterised by a high conversion of the monomer (97%) with selectivity of linear dimers of α-methylstyrene (4-methyl-2,4-diphenylpent-1- and -2-enes) 94% in the presence of these catalysts under mild conditions ($p = 0.1$ MPa, $T = 75–100$ °C).

Analogous results were obtained while studying of α-methylstyrene linear dimerisation in the presence of zeolites of Y, Beta, ZSM-12 [16–22].

In contrast to the wealth of detailed studies on the dimerisation of individual monomers, the codimerisation of styrene and α-methylstyrene has not been thoroughly investigated. Styrene and α-methylstyrene codimerisation in the presence of phosphoric acid has been reported; the conditions led to a mixture of cyclic homo- and codimers. The synthesis was carried out at 130–155 °C using phosphoric acid, which was concentrated through evaporation (until the boiling point 200–220 °C), and a mixture of monomers (monomers:$H_3PO_4 = 1:2$, w/w) [23]. We chose, instead, to study styrene/α-methylstyrene codimerisation using heterogeneous catalysts.

The successful synthesis of homodimers of styrene and α-methylstyrene in the presence of zeolite catalysts lead us to assume that zeolites may also be useful in the production of vinylarene codimers mentioned above.

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Nomenclature

α-ms	α-methylstyrene
CD	cyclic dimer
CCD	cyclic codimer of styrene and α-methylstyrene
LCD	linear codimer of styrene and α-methylstyrene
LD	linear dimer
$[M_0]$	initial vinylarenes concentration in chlorbenzene
MWD	molecular-weight distribution
St	styrene
T	temperature

This study of the reaction of styrene and α-methylstyrene in the presence of the large-pore zeolites Y and Beta and medium-pore ZSM-12 will help develop a low-waste method of vinylarene cooligomerisation.

2. Experimental

2.1. Chemicals and materials

Rectified styrene (public corporation "Salavatnefteorgsyntez", 99.9%), α-methylstyrene (public corporation "Ufaorgsyntez", 99.8%) and chlorobenzene (Acros Chemicals, 99.9%) were used.

2.2. Catalysts

Zeolite Y, with a SiO_2/Al_2O_3 ratio = 6.0, was synthesised in the Na-form by a previously described technique [24]. Zeolite NaY was transformed into the H-form (exchange degree of ions Na^+ on H^+ was 96%) by decationation from a solution of NH_4NO_3 in three stages and by intermediate calcination at 540 °C. Zeolites NH_4-Beta (BEA) and H-ZSM-12 (MTW) were produced by the public corporation Angarsk Factory of Catalysts and Organic Synthesis. Zeolite NH_4-Beta was transferred into H-form by calcination at 540 °C for 4 h. Catalyst characteristics are collected in Table 1, FTIR-spectra in Fig. 1. The FTIR-spectra were recorded at the Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences. Catalyst samples were calcined at 540 °C for 4 h before all experiments.

2.3. Cooligomerisation of vinylarenes

Cooligomerisation was carried out in a isothermal batch reactor in the presence of 5–20 wt.% of catalyst (calculated on mixture of vinylarenes), at 80–130 °C, in the presence or absence of chlorobenzene. After the completion of the reaction, the reaction mass was separated from the catalyst by filtration. The conversion of initial vinylarenes and the quantitative composition of the dimer fraction were determined using gas-liquid chromatography (GLC). The composition of the oligomers formed was analysed using high-performance liquid chromatography (HPLC). For calibration, dimers and trimers were isolated with vacuum distillation.

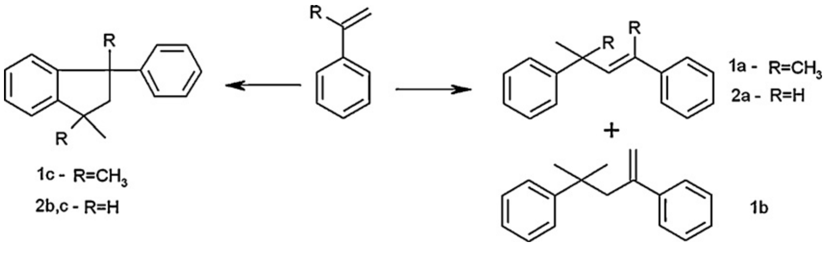
Homodimers of styrene and α-methylstyrene (**1, 2**) were identified using presynthesised compounds [25,26]. The chemical structure of codimers (**3, 4, 6**) was established by means of GC/MS and NMR spectroscopy; linear codimers (**5**) were identified using GC/MS-spectrometry.

2.3.1. *Synthesis of trans-3-methyl-1,3-diphenylbut-1-ene and 2,4-diphenylpent-1-ene (Scheme 2)*

Zeolite HZSM-12 (1.1 g) was added to a mixture of styrene (5.2 g, 5 mmol) and α-methylstyrene (5.9 g, 5 mmol) in chlorobenzene (25 ml) at 100 °C and stirred for 5 h. After cooling, the catalyst was filtered from the reaction mixture and solvent, and unreacted vinylarenes were removed at reduced pressure. Dimer fractions (8.5 g) (120–135 °C/2 mm Hg) were isolated through distillation of the reaction mixture (dimers – 82.2%, trimers and higher molecules – 17.8%). Cyclic dimers **1c, 6** (60%) were separated by means of recrystallisation of dimer fractions from ethanol. The concentrate of linear homo- and codimers was distilled under vacuum. The fraction with the highest linear codimer content (1,3-diphenylbut-1-ene **2a** (11.7%); 4-methyl-2,4-diphenylpent-1-ene **1a** (7.7%); 4-methyl-2,4-diphenylpent-2-ene **1b** (30.8%); **3** (21.5%); **4** (28.3%) was analysed using ^1H and ^{13}C NMR.

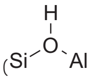
***trans*-3-Methyl-1,3-diphenylbut-1-ene (3)**. ^1H NMR, δ: 1.70 (6 H, s, $2CH_3$), 6.60–6.65 (2H, m, $J = 10$, CH=CH), 7.0–7.6 (10H, m, ArH); ^{13}C NMR, δ: 28.89 (CH_3), 40.94 (CH), 126.09 (=CH), 140.30 (=CH); 121.91–148.73 (Ar); m/z: 222; Kovaè index I_k 1820

2,4-Diphenylpent-2-ene (4). ^1H NMR, δ: 1.60 (3H, d, J 7.0, CH_3), 2.26 (3H, s, CH_3), 4.03 (1H, m, CH), 6.11 (1H, d, =CH), 6.95-7.43 (10H, m, ArH); ^{13}C NMR, δ: 16.26 (CH_3), 22.61 (CH_3), 38.47 (CH),



Scheme 1. Homo-dimerisation of styrene and α-methylstyrene.

Table 1
Characteristics of zeolites.

Catalyst	SiO_2/Al_2O_3 ratio	Degree of exchange of Na^+ for H^+ (%)	Degree of crystallinity (%)	Acid properties		
				N_H, (μmol g^{-1})	PA (kJ mol^{-1})	References
Y	6	96	100	320 ( $Si-\overset{H}{O}-Al$)	1170	[18]
				60 (AlOH)	1220	
				73 (AlOH)	1265	
Beta	18	98	99	179	1165	[19]
ZSM-12	34	98	100	106	1165	[19]