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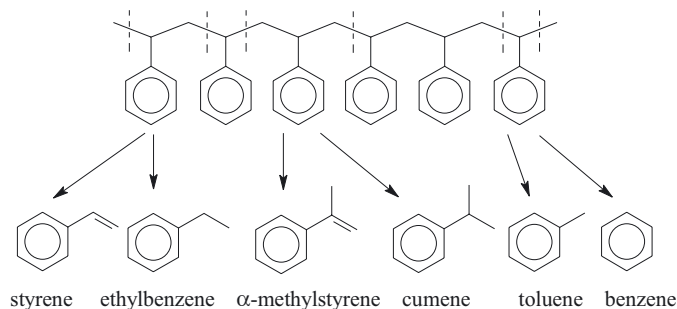
Catalytic degradation of polystyrene

RAPID COMMUNICATION

Summary — Syndiotactic polystyrene was degraded in an atmosphere of N₂ or H₂ at 375 or 400 °C in the presence of transition metal catalysts (Cr, Ni, Mo, Co or Fe) on the support (Al₂O₃, SiO₂). Styrene, ethyl benzene, α -methylstyrene, cumene, toluene, benzene as well as bi- and tricyclic hydrocarbons were found in the reaction products. Effects of degradation conditions on the products compositions were discussed. The highest yield of styrene monomer (>80 %) was reached when iron-based catalysts were used.

Key words: syndiotactic polystyrene, catalytic depolymerization, catalysts, transition metal, support, yield of styrene.

Polystyrene (PS) belongs to the group of vinyl polymers which can be thermally depolymerized to afford monomers in substantial yields. Thermal degradation of PS is radical in nature and is the result of breaking of C-C bonds in polymer chains. The primary reaction of PS depolymerization (Scheme A) led not only to styrene, but also to α -methylstyrene, toluene and benzene and it



Scheme A. Thermal degradation of PS

was accompanied by secondary reactions of hydrogen transfer resulting in the formation of ethyl benzene, cumene as well as di-, tri- and polycyclic compounds. Furthermore, triphenylbenzene, diphenylpropane, diphenylbutene and triphenylhexene (styrene oligomers) were found in the products of PS degradation. Both pyrolysis and hydrolysis of PS yielded a broad non-specific spectrum of volatile products. This fact is of particular importance for exploring the possibilities of recovering styrene by recycling of PS wastes [1, 2].

Thermal depolymerization of PS under industrial conditions usually recovered styrene monomer in yields of only 40–70 % [3] and can hardly be considered as an efficient method of recovering pure monomer from PS wastes.

Recently, Krauze *et al.* [4] have qualitatively studied thermal degradation of PS in air or nitrogen in relation to temperature (300 °C to 600 °C). In the nitrogen atmosphere, styrene was found to be preferentially formed at the low reaction temperature, whereas, at 600 °C, substantial amounts of toluene, ethylbenzene, α -methylstyrene, diphenylpropane, 1,2-diphenylethylene, styrene dimer, 1,4-diphenyl-1,3-butadiene, 2-phenylnaphthalene, and *m*-terphenyl were found to have been additionally formed. Under air atmosphere, some oxygen-containing compounds (carbon dioxide, benzaldehyde, phenol and α -tolylaldehyde) as well as bibenzyl, were found to occur in the reaction products. When the reaction was carried out under air atmosphere, the products of degradation were more complex than those formed under nitrogen one. Thermogravimetric data showed the conversions of PS to volatile compounds equal 98 % in nitrogen, but only 92 % in an air.

Catalytic degradation of PS under hydrogen atmosphere was studied by Zmierczak *et al.* [5] a few years ago. As catalysts, solid superacids [sulfated zirconia or iron(III) oxide] were used at 350–450 °C and hydrogen pressure 500–2500 psi (3.44–17.2 MPa) for 12–120 min. The conversion of PS increased from 61 % to 96 % when the temperature, hydrogen pressure and reaction time were increased. No styrene was found in the product. Ethylbenzene, toluene, C₃-alkylbenzenes and

diphenylpropanes were the main products of the degradation.

Degradation of PS under the conditions conducive to hydrogen transfer has been also studied by J. Polaczek *et al.* [6]. Coal tar pitch solutions of PS were heated at 300–500 °C for 2–3 h under nitrogen atmosphere. Heating of a coal tar pitch resulted in the formation of free hydrogen as by-product to the formation of polycyclic aromatic structures by polycondensation. Under such conditions, ethylbenzene was the main component of the volatile products of degradation (56 %). The content of styrene was substantially lower (14 %), close to that of cumene and toluene (13 % each). The content of α -methylstyrene was negligible (4 %). Unfortunately, neither bi- nor tricyclic compounds were determined in the reaction product.

In this connection we found important, from the practical point of view, to study the effects of some selected catalysts (typical for petrochemical conversion of hydrocarbons) on the course of PS degradation at the initial and middle stages of the reaction (conversion degrees from 30 % to 90 %).

EXPERIMENTAL

Materials

The following materials have been used:

— syndiotactic polystyrene (average molecular weight M_w 176 000 g/mol, polydispersity 2.6, stereoregularity index 96.7 %, particle size 2.5 mm) was supplied by the Industrial Chemistry Research Institute, Warsaw;

— $Mg(NO_3)_2 \cdot 6H_2O$ — pure *pro analysi*, $Co(NO_3)_2 \cdot 6H_2O$ — pure *pro analysi*, $Fe(NO_3)_3 \cdot 9H_2O$ — pure *pro analysi*, $Ni(NO_3)_2 \cdot 6H_2O$ — pure *pro analysi*, $(CH_3COO)_2Ni$ — pure *pro analysi*, and $H_2MoO_4 \cdot H_2O$ — pure *pro analysi* (POCh, Gliwice, Poland);

— NaOH — pure *pro analysi* (HEMPUR, Piekary Śląskie, Poland);

— technical-grade nitrogen gas and pure-grade hydrogen gas (MULTAX s.c., Zielonki-Parcela, Poland);

— technical-grade liquid nitrogen (produced at the Institute for Opto- and Microelectronics, Warsaw University of Technology);

— Al_2O_3 — pure *pro analysi* (Degussa's Alumina C);

— SiO_2 — pure *pro analysi* (Degussa 200);

— TiO_2 — pure *pro analysi* (Degussa P-25);

— Ni-Mo/ Al_2O_3 (BASF, Germany);

— Co-Mo/ Al_2O_3 (BASF, Germany).

Preparation of catalysts

Cr_2O_3/Al_2O_3 catalyst was prepared by wet-impregnating of γ - Al_2O_3 with aqueous chromium nitrate, drying at 120 °C for 12 h and subsequent calcination of the impregnate at 550 °C for 5 h.

Catalysts Ni/ Al_2O_3 , Co/ Al_2O_3 and Mo/ Al_2O_3 were prepared by wet-impregnating of the carrier with aqueous nickel(II) or cobalt(II) nitrate or with molybdic acid and drying of each impregnate in an air at temperature of 120 °C for 12 h. After calcination at 550 °C for 5 h, the precatalyst samples were reduced with hydrogen at 550 °C for 1 h. The mass of the metal deposited was 5 % of the catalyst mass.

MgO catalyst was prepared by precipitating of magnesium hydroxide from magnesium nitrate and ammonia solutions, ageing of the hydroxide for 14 days, decanting, and drying the precipitate at temperature of 50, 80, 100 and 120 °C (2 h at each temperature).

Catalyst Fe/ SiO_2 was prepared by wet-impregnating of SiO_2 with aqueous iron(III) nitrate and drying of the impregnate in an air at temperature of 120 °C for 12 h. The mass of iron was 5 % of the catalyst mass.

To prepare Fe-Co/ SiO_2 catalyst, aqueous iron(III) nitrate and cobalt(II) nitrate were applied to the surface of SiO_2 in such amounts that Fe and Co were respectively 2 % and 18 % (CoO weight basis) of the catalyst mass, and then dried in an air at temperature of 120 °C for 12 h.

To prepare Ni-Fe-Co/ SiO_2 catalyst, aqueous nickel acetate was applied to the above-mentioned Fe-Co/ SiO_2 catalyst in such amount that Ni was 0.5 % of the catalyst mass and the impregnate was dried at 120 °C for 12 h.

The procedures of calcination and reduction of iron-containing catalysts were the same as in the case of Ni, Co and Mo catalysts.

Apparatus

PS was degraded in 100-mL glass reactor (Fig. 1) which was kept in an oven which temperature was controlled with ASH-2 thermoregulator equipped with Fe-Cu-Ni thermocouple. Additionally, a comparative thermocouple Fe-Cu-Ni was used. The thermoregulator was operated in conjunction with AI-2500 laboratory autotransformer. Nitrogen (or hydrogen) was distributed from a cylinder through a rheometer followed by an additional control valve. Reaction products were collected in a receiver connected with the reactor and cooled with a liquid nitrogen.

Method of investigations

Syndiotactic PS (1 g), and a freshly prepared catalyst (0.2 g, particle size 1.25 mm) were placed in the reactor with nitrogen allowed to pass continuously. The catalyst was calcinated for 12 h in an air stream at 550 °C and for 1 h in an atmosphere of nitrogen at 550 °C. The reactor was placed in the heating oven. The reaction was run for 1.5 h at 375 °C or 400 °C in a stream of nitrogen. In a few cases nitrogen was substituted with hydrogen.

For some metal catalysts, the method used to run the reaction was somewhat modified. Prior to the reaction, the catalysts Ni/ Al_2O_3 , Co/ Al_2O_3 , Mo/ Al_2O_3 were addi-

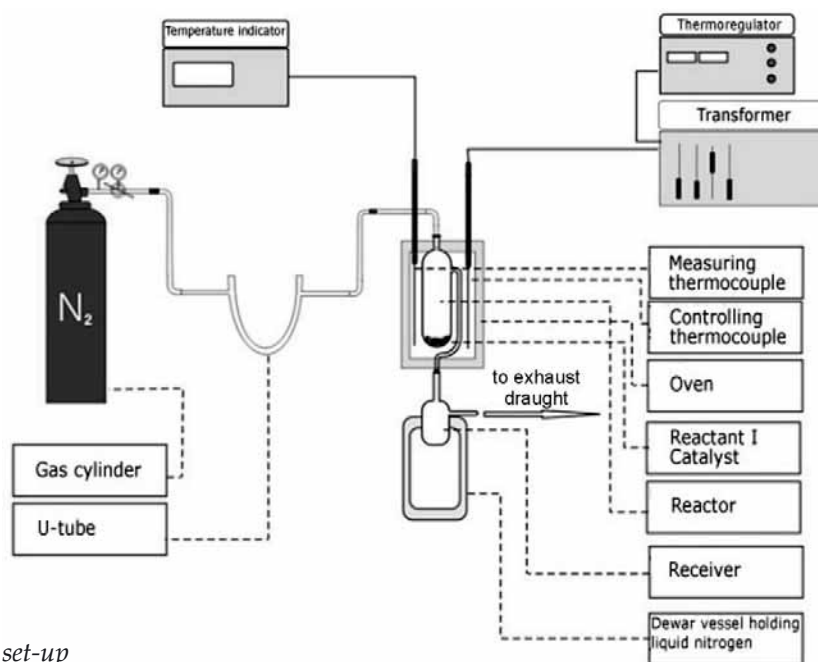


Fig. 1. The experimental set-up

tionally pre-reduced for 1 h at 550 °C. Nitrogen was used as a product-carrying gas.

Additional reactions were also carried out over Fe/SiO₂, Fe-Co/SiO₂, Ni-Fe-Co/SiO₂, and Co-Mo/Al₂O₃. Prior to the reaction, each of these catalysts was also pre-reduced with hydrogen. And again hydrogen was used as a product-carrying gas.

For comparison, at each experimental temperature the reaction was run with no catalyst used.

Analysis of reaction products

CHROM 5 gas chromatograph operated in conjunction with a mass spectrometer was used to analyze the liquid products of the reactions.

RESULTS AND DISCUSSION

Results of the study are collected in Tables 1 and 2.

First of all, under nitrogen atmosphere, the yield of the monocyclic compounds was found to increase over alumina-supported catalyst as the reaction temperature was raised. In contrast, over the magnesium oxide and silica-supported catalysts, the yields were found to decrease.

The transition metals-containing catalysts, especially those containing molybdenum, exhibited an activity in the hydrogen transfer reactions leading to saturated side-chain hydrocarbons (ethyl benzene, cumene) both at 375 °C and 400 °C. This activity of the molybdenum-containing catalysts remained unchanged when the catalysts were hydrogen-treated before use or when they were used under hydrogen atmosphere. The degree of styrene recovery increased when hydrogen-treated catalysts were used but significantly decreased when the degradation was carried out in hydrogen atmosphere. In

both cases, the contents of di- and tricyclic compounds were considerable lower than those in the products obtained under nitrogen atmosphere.

CONCLUSIONS

Metal oxide and metal oxide-supported transition metal catalysts (commonly used for processing of the petroleum-derived hydrocarbon fractions) generally resulted in a diminished degree of PS conversion but in an increased content of monocyclic hydrocarbons in the volatile products. Metal oxides were less catalytically active than metal oxide-supported transition metals.

An increase in the degradation temperature resulted in general both in a higher degree of conversion and in a higher content of bi- and tricyclic hydrocarbons in the volatile products of PS degradation. This means, the rates of secondary reactions rose when the reaction temperature increased.

The hydrogen atmosphere contributed to the formation of saturated aromatic hydrocarbons in keeping with the earlier observations by Zmierczak *et al.* [5]. The yield of monocyclic aromatic hydrocarbons considerably increased under hydrogen atmosphere, while the yields of high boiling bi- and tricyclic aromatic hydrocarbons dropped. Use of hydrogen results, however, results in a dramatic increase in processing costs and can not be recommended for any commercial use in the case of PS waste degradation. Therefore, only selected gamma-alumina and silica-supported catalysts were tested under hydrogen atmosphere for comparison purposes.

The iron catalyst showed an enhanced catalytic activity and selectivity in styrene monomer recovery from PS. This observation can be helpful in chemical recycling of PS wastes [7].

Table 1. The composition (in wt. %) of the volatiles formed during catalytic decomposition of PS at 375 °C and 400 °C in nitrogen atmosphere

Temp. °C	Depolymerized products, wt. %	No catalyst	Catalyst												
			TiO ₂	γ-Al ₂ O ₃	Cr ₂ O ₃ /Al ₂ O ₃	Ni/Al ₂ O ₃	Mo/Al ₂ O ₃	Co/Al ₂ O ₃	Ni-Mo/Al ₂ O ₃	Co-Mo/Al ₂ O ₃	MgO	SiO ₂	Fe/SiO ₂	Fe-Co/SiO ₂	Ni-Fe-Co/SiO ₂
375	Monocyclic compounds including:	66.0	67.2	75.7	65.2	74.6	74.6	78.2	70.1	77.3	67.3	65.9	84.7	80.5	74.7
	styrene	59.6	49.1	60.6	57.4	63.7	37.2	61.7	36.3	44.7	59.6	59.7	73.6	68.7	63.2
	ethylbenzene	—	5.6	2.0	—	—	19.7	—	18.5	18.8	—	—	—	—	—
	α-methylstyrene	0.9	1.3	1.2	1.0	1.2	0.5	0.9	0.6	0.9	1.1	0.8	2.0	1.4	—
	cumene	1.7	5.3	5.4	2.5	3.6	8.4	3.5	7.0	5.4	0.9	1.4	4.9	6.0	7.8
	toluene	3.0	3.5	5.3	2.8	4.2	5.5	11.0	3.9	4.8	3.6	3.4	3.6	3.8	2.9
	benzene	—	0.8	0.3	0.1	0.1	2.7	—	2.1	1.9	0.9	—	0.1	0.1	—
	other	0.8	1.6	0.9	1.4	1.8	0.6	1.1	1.7	0.8	1.2	0.6	0.5	0.5	0.7
	Bicyclic compounds	12.6	14.5	11.1	19.0	11.0	19.6	8.7	16.1	12.7	13.7	11.6	5.6	6.8	9.8
	Tricyclic compounds	21.4	18.3	13.2	15.8	14.4	5.8	13.1	13.8	10.0	19.0	22.5	9.7	12.7	15.5
400	Monocyclic compounds including:	66.2	74.1	77.4	69.9	74.9	81.0	72.4	70.9	72.6	65.2	64.0	80.1	71.9	73.6
	styrene	57.9	56.5	61.2	58.8	63.2	41.4	62.7	45.1	43.6	57.8	58.5	63.9	60.6	60.2
	ethylbenzene	—	4.6	2.9	1.4	—	21.6	—	12.9	15.5	—	—	1.3	0.8	0.9
	α-methylstyrene	0.8	1.0	0.9	0.5	0.8	0.4	0.8	0.7	0.7	1.0	0.4	1.0	0.8	0.8
	cumene	2.7	6.8	6.5	3.8	5.5	7.2	4.0	6.2	7.7	1.7	2.1	8.7	5.7	6.9
	toluene	3.1	3.9	5.2	4.5	4.4	6.8	4.0	3.7	3.9	3.5	2.8	4.6	3.5	4.3
	benzene	—	0.5	0.3	0.1	0.2	3.4	—	1.2	0.9	0.3	—	0.1	0.1	0.2
	other	1.7	0.8	0.4	0.8	0.8	0.2	0.9	1.1	0.3	0.9	0.2	0.5	0.4	0.3
	Bicyclic compounds	12.6	15.3	11.1	13.3	10.1	11.9	9.9	14.1	15.8	12.0	12.3	10.2	11.1	9.6
	Tricyclic compounds	21.2	10.6	11.5	16.8	15.0	7.1	17.7	15.0	11.6	22.8	23.7	9.7	17.0	16.8

Table 2. The composition (in wt. %) of the volatiles formed during catalytic decomposition of PS at 375 °C in hydrogen atmosphere

Depolymerized products, wt. %	Hydrogen—pre-reduced catalyst			Reaction run in hydrogen atmosphere			
	Ni/Al ₂ O ₃	Mo/Al ₂ O ₃	Co/Al ₂ O ₃	Co-Mo/Al ₂ O ₃	Fe/SiO ₂	Fe-Co/SiO ₂	Ni-Fe-Co/SiO ₂
Monocyclic compounds including:	83.1	84.0	79.5	85.6	82.4	85.7	81.7
styrene	69.8	47.4	71.7	42.9	54.6	36.7	28.4
ethylbenzene	—	21.7	—	31.8	8.8	24.5	31.0
α-methylstyrene	1.0	1.2	0.8	0.5	1.2	0.5	2.0
cumene	4.4	5.1	3.6	2.7	9.1	6.0	5.4
toluene	5.0	5.4	2.6	5.6	5.1	11.4	8.3
benzene	1.6	2.7	—	1.6	2.3	5.8	5.6
other	1.3	0.5	0.8	0.5	1.3	0.8	1.0
Bicyclic compounds	9.9	10.4	9.0	8.4	11.9	8.9	9.8
Tricyclic compounds	7.0	5.6	11.5	6.0	5.7	5.4	8.5

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Received 13 VIII 2004.