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MODIFICATION IN THERMAL DECOMPOSITION PRODUCTS OF POLYMERS BY CATALYTIC PYROLYSIS

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ABSTRACT

The catalytic pyrolysis of various hydrocarbon polymers such as aliphatic saturated, olefinic and aromatic compounds was studied in order to investigate the influence of catalysts on the composition of decomposition products. The following types of catalysts were used: pure metals, metal oxides, zeolites and amorphous or crystalline silicates. The order of efficiency of these catalysts for the recovery of polymers was also established.

INTRODUCTION

The catalytic thermal decomposition of polymers has hardly been studied. Some mention has been made with respect to the erroneous results of thermal analysis, or the modification of the reaction kinetics. But the energy crisis and lack of raw materials in the last decade determined the necessity of efficient recovery of various secondary resources. Thus the recovery of secondary polymeric materials (SPM) by using catalytic pyrolysis became a new research field by the beginning of the ninth decade.

This paper shows mainly a comparison between the effects of various catalysts on the thermal decomposition of polymeric materials like polyethylene, polypropylene, styrenic polymers and vulcanized and unvulcanized rubbers.

EXPERIMENTAL

The study was carried out on both pure and impurified polymers like polymeric wastes and aged plastics. The following catalysts were tested: aluminium bronze, MnO_2 on fire bricks, Cr_2O_3 on asbestos, CuO on fire bricks and asbestos, silica alumina amorphous catalysts with 13% and 25% Al_2O_3, silica-alumina crystals with 10-20% molecular sieves, macroporous mordenits with 15% Al_2O_3,

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microporous mordenits with 12% Al_2O_3 and ZSM-5 zeolites which contain 2.6% Al_2O_3. The pyrolysis experiments were carried out in two steps, one at 400-500°C and the second at 420-500°C. The catalysts were used as a fixed bed.

The pyrolysis products mixtures were characterized both like complete products and like fractions of 10-20°C boiling range. The identification of functional groups was made by means of ^{1}H-NMR, IR and UV-Visible spectra and using the specific reactions with urea and thiourea. Many components were determined by gas-chromatography. Other characteristics determined were: density, refraction index, molecular weight, etc.[1].

RESULTS AND DISCUSSION

Besides the well known radical decomposition, the catalysts induce many secondary reactions, such as intermolecular hydrogen extraction, isomerization at double bonds, branchings, alkylation, cyclization and aromatization, dehydrogenation, secondary crackings and destructive scission, polymerization, coking[2].

Contrary to non-catalytic thermal decomposition, the catalysts cause an increase in the amount of gas (Table 1) and the fluidity (the viscosity and softening points decrease) of the condensable fraction, and a 5-10% deposition of coke on the catalyst.

Depending on the chemical composition and pore structure of catalysts, some secondary reactions are favoured against others. For example, the amorphous alumina-silica catalysts and the mordenits favour equally the appearance of unsaturated and aromatic compounds. On the other hand, the ZSM-5 zeolites induce a high aromatization tendency, so that the liquid (T_b=120-140°C) fractions of pyrolysis products of polyethylene or polypropylene contain practically aromatic components only (Fig.1).

The non-catalytic thermal decomposition of styrenic polymers leads to important quantities of styrene monomer and oligomers, the monomer percentage being 30-40%. If the process is catalysed, the proportion of oligomers is very much lower and the content of valuable products becomes important. For example, the CuO catalyst favours the formation of styrene monomer, while silicate catalysts determine a high content of ethylbenzene. It is quite probable that ethylbenzene is formed by a hydrogenation of styrene monomer. Such a process is also characteristic for other studied polymers.

TABLE 1

The quantities of the gaseous and condensable products resulting from catalytic pyrolysis

Nº	Sample	GASEOUS PRODUCT			CONDENSABLE PRODUCT		
		PE and PP	Styrenic polymers	Un- and vulcanized elastomers	PE and PP	Styrenic polymers	Un- and vulcanized elastomers
1.	Uncatalytic	8-9	1.3-5	4.5-3.7	92-91	94-90	90-64
2.	Aluminium bronze	9-10	1.4-4	4.5-4.4	88-87	92-89	91-61
3.	MnO_2/K_2O/firebrick	12-13	1.6-3.7	4.7-4,0	62-70	91-87	91-62
4.	Cr_2O_3/K_2O/asbestos	12-13	1.8-3	5-4.7	70-74	91-87	89-62
5.	CuO/firebrick	20-21	1.5-2.7	5-4.4	75-73	92-88	90-60
6.	CuO/asbestos	24-25	1.8-4	5-4.8	65-67	92-86	89-62
7.	Amorphous silica alumina 13%Al_2O_3	18-22	9.2-6	9.4-8.2	66-74	90-86	85-58
8.	Amorphous silica alumina 25% Al_2O_3	35-37	12-14	9.8-8.9	56-58	81-76	85-58
9.	Crystalline silicate 10% molecular sieves	37-38	14-17	12-10	51-53	80-73	83-50
10.	Microporous mordenite	16-24	5.4-9.4	9-8	66-78	88-81	81-56
11.	Macroporous mordedenite	20-27	6.9-18	12-11	69-71	87-72	84-51
12.	ZSM-5	42-44	10-12	14-12	48-59	83-79	64-40

PE and PP: low and high pressure polyethylene, atactic and isotactic polypropylene;
Styrenic polymers: polystyrene, ABS copolymers and their mixtures;
Unvulcanized and vulcanized elastomeres: Styrene or α-methylstyrene butadiene copolymers and tires.

The obtained results indicate the following order for the efficiency of the catalysts tested: aluminium bronze <MnO_2<Cr_2O_3<CuO<UC-non-catalytic; C-catalytic<microporous mordenits<macroporous mor-

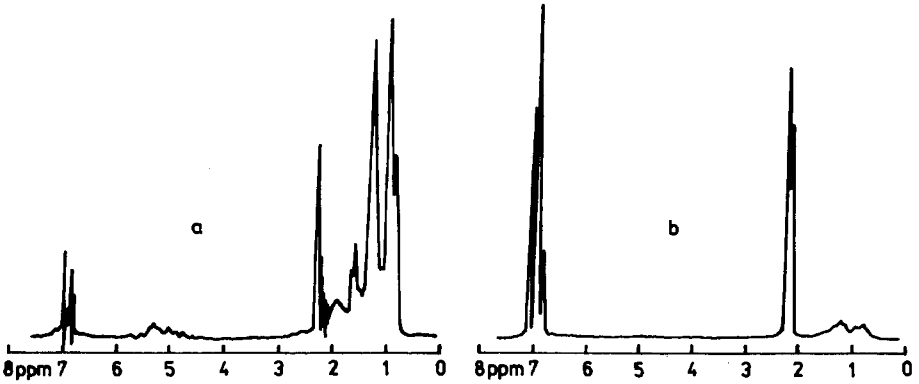

Fig.1. ^{1}H-NMR spectra of the fraction with 130-136°C boiling interval for the catalytic decomposition products of PE over alumina silica (a) and ZSM-5 (b) catalyst.

TABLE 2

Pyrolytic ways to recovery of SPM

SPM	Procedure	Obtained Products
PE and PP	UC	-Waxes with board distribution of molecular weight -Lubreficants -Carburants
	All catalysts	-Gases with high content of monomer which is returned in synthesis -Lubreficants -High grade carburants -Raw petrochemical materials
	C/ZSM-5	-Aromatics -High grade carburants
Styrenic Polymers	UC	-Styrene very difficult to return in synthesis due to the presence of oligomers
	C/CuO	-Styrene which is easy recyrculated in synthesis

Used tires and others elastomeric wastes	UC	-Heavy fractions for retarded coking
	C/ZSM-5	-Aromatics
SPM from polymer mixtures	UC	-Complex mixtures very difficult to use -Coke
	C/silicat catalyst on ZSM-5	-Synthetic oil,raw petrochemical materials -Black carbon

denits<amorphous alumina-silica (13% Al_2O_3)<amorphous alumina-silica (25% Al_2O_3)<crystalline silicates (10% molecular sieves)< ZSM-5 zeolites.

Another interesting conclusion is that the efficiency of catalysts is not affected if the polymers are impurified with chemical fertilizers, surface agents, dimethylterephtalate, cellulosic materials, black carbon, sulphur [3]. Hence the procedures in Table 2 are proposed for an efficient recovery of polymeric wastes.

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