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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Distribution of Heteroatoms of Synthetic Ion Exchangers in Pyrolysis Products

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Abstract—Distribution of sulfur and nitrogen atoms in products of pyrolysis of spent synthetic ion exchangers AV-17 and KU-2 in the temperature range 50–550°C was studied. The compounds containing heteroatoms were identified, and their amounts were determined.

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Involvement of production and consumption wastes in economy as secondary raw materials provides resource saving and environmental protection. Wastes containing synthetic polymers are considered as raw materials for production of a wide assortment of materials and articles for various purposes. However, considerable amounts of polymer-containing wastes are disposed of on disposal sites of industrial and municipal wastes, thus considerably reducing the capacity of these sites.

The majority of studies and practically implemented technologies for polymer waste reprocessing deal with thermoplastic materials. However, wastes containing network polymers cannot be reprocessed into materials and articles by methods developed for thermoplastics. Spent synthetic ion-exchange resins are among materials for which reprocessing technologies have not yet been developed. Up to now, spent synthetic ion exchangers were not considered as secondary raw material.

Ion-exchange materials are used in water treatment processes, in hydrometallurgy, in electroplating, in food, hydrolysis, and chemical industries, as catalysts of various chemical processes, in analytical chemistry, in medicine, in biology, and in pharmaceutical industry [1]. The operation life of ion exchangers is limited by a decrease in the exchange capacity and by the loss of the shape (wear, cracking, etc.).

Spent ion exchangers find no use today and are disposed of on special sites. In contrast to polymeric materials, spent ion exchangers contain no fillers, pigments, stabilizers, and reinforcing components. Therefore, they can be considered as a promising material for pyrolytic reprocessing. The products obtained can be used as chemical raw materials; fractions containing no sulfur and nitrogen heteroatoms, as fuel or fuel additives; and the solid residue, if it exhibits sorption properties, as a sorbent.

The functional groups of the most widely used synthetic ion exchangers contain nitrogen and sulfur. The distribution of heteroatoms among the solid, liquid, and gas fractions formed by pyrolysis of spent ion exchangers strongly affects the choice of their further applications and the environmental parameters of the process.

Our experiments were performed with spent strongly basic anion exchanger AV-17×8 and strongly acidic cation exchanger KU-2×8, used in water treatment for softening and desalination of river water.

In this study we examined how the conditions of thermal degradation of spent synthetic ion exchangers affect the distribution of heteroatoms of functional groups.

EXPERIMENTAL

In our studies we used differential thermal analysis (DTA; TA Instrument device, USA; nitrogen atmosphere; heating rate 10 deg min^{-1}; determination accuracy: temperature ±0.01°C, enthalpy ±0.01 J g^{-1}) and differential scanning calorimetry (DSC 2010 device, Du

Pont, equipped with a thermal cell with compartments for the reference sample and test compounds). The elemental composition was determined by combustion of the samples, followed by gas-chromatographic analysis of oxidation products with a CHNS analyzer (Elementar Vario EL III) equipped with a thermal conductivity detector. The composition of liquid fractions was determined by gas chromatography using flame ionization and mass spectrometric detectors (HP 6890 Series GC System) with a detection limit of 4 pg cm^{-3} and a 0.32 mm Ч 60 m capillary column coated with SE-30. The flow rates of the carrier gas (nitrogen), air, and hydrogen were 30, 300, and 28 cm^3 min^{-1}, respectively. The column, detector, and vaporizer temperatures were 50–200 (heating rate 5 deg min^{-1}), 240, and 300°C, respectively. The total static sorption capacity (TSSC) was determined by sorption of Cu^{2+} for the cation exchanger and Cl^- for the anion exchanger [2], and also by sorption of dyes from aqueous solutions [3]. The content of sulfur-containing gases in gaseous products was determined by turbidimetry (SO_2, SO_3), potentiometric titration, and nephelometry (H_2S) [4].

Heat treatment of spent ion exchangers was performed in an electrically heated cylindrical steel vessel (55 mm in diameter, 240 mm long). The weight of the spent ion exchanger sample was 50 g, and the nitrogen consumption, 5 l min^{-1}. The products formed in the course of heat treatment were removed from the reactor with a nitrogen flow and passed successively through a water-cooled condenser, a separator, and an absorber with water to absorb water-soluble components.

As a result of heat treatment of spent ion exchangers, we obtained a solid residue and liquid and gaseous products.

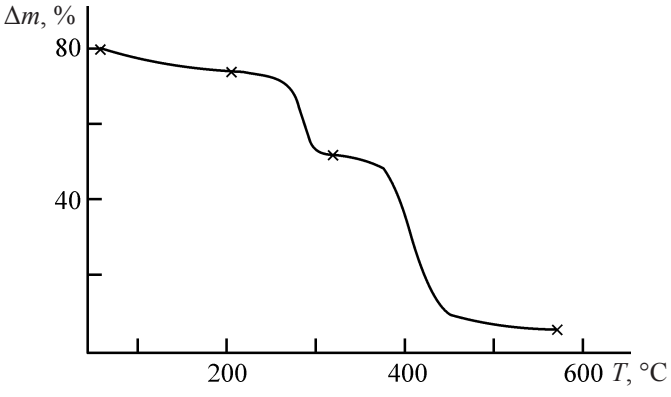

Fig. 1. Thermogram of the spent anion exchanger. (Δ*m*) Weight loss and (*T*) temperature; the same for Fig. 2.

Total static sorption capacity

Treatment temperature, °C	TSSC of solid residue			
	KU-2×8 for copper	AV-17×8 for chlorine	KU-2×8 for Methylene Blue	AV-17×8 for Acid Blue
	mg-equiv g^{-1}		mg g^{-1}	
100 ± 5	2.08	1.00	12.32	20.7
150 ± 5	1.99	0.50	8.15	12.3
250 ± 5	1.94	0.07	5.13	8.4
350 ± 5	1.90	0.00	5.07	4.9
550 ± 5	1.78	0.00	3.27	4.9

Analysis of the initial and spent synthetic ion exchangers showed that the spent anion exchanger is characterized by a lower content of nitrogen in quaternary ammonium groups (13.8 wt % relative to the initial content). The sulfur content of the cation exchanger does not appreciably change in the course of service (decrease by 3.5 wt % relative to the initial content). However, the exchange capacity of the spent resins (both cation and anion exchangers) appeared to be lower by a factor of 2 than that of the initial resins. This fact suggests that the functional groups may be blocked by humic and fulvic acids and by other substances.

The energy of carbon–heteroatom bonds in ion exchanger macromolecules is lower than that of carbon–carbon bonds C–S 138, C–N 334, C–O 376, C_{ar}–C_{alk} 384, C=C 588, and C_{ar}–C_{ar} 610 kJ mol^{-1}. Therefore, presumably, cleavage of specifically these bonds will determine the onset temperature of thermal degradation [2].

The thermograms and DSC patterns of the samples show that the anion and cation exchangers significantly differ in the heat resistance [5]. In the TGA curves of the spent anion exchanger (Fig. 1), there are three steps of

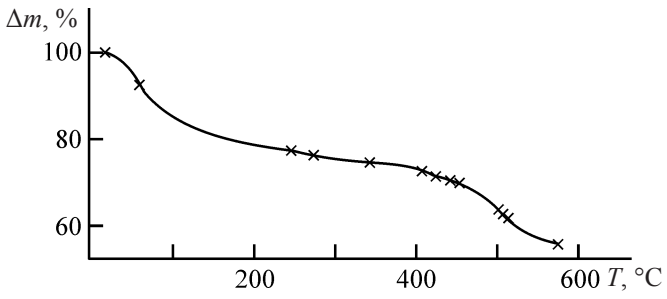

Fig. 2. Thermogram of the spent cation exchanger.

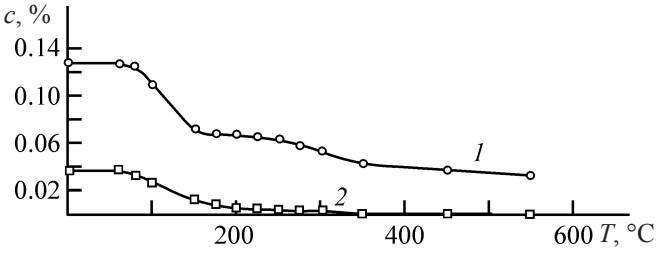

Fig. 3. Content c of heteroatoms in the solid residue after heat treatment of spent ion exchangers, as a function of temperature *T*.

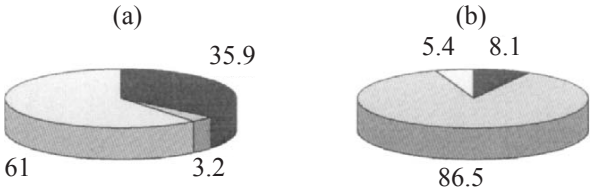

Fig. 4. Distribution of heteroatoms among fractions from heat treatment of ion exchangers: (a) S and (b) N. Fraction: (*1*) solid, (*2*) liquid, and (*3*) gas.

the weight loss: removal of bound water, sorbed gases, and nitrogen-containing compounds (50–210°C); release of nitrogen-containing compounds only (210–320°C); removal of hydrocarbons formed by degradation of the hydrocarbon matrix (320–480°C).

The spent cation exchanger is characterized by a more complex and multistep thermal degradation process (Fig. 2). The removal of bound water and sorbed gases is accompanied by removal of sulfur in the form of SO_2 as a result of cleavage of C–S bonds in the temperature range 240–340°C and by successive reactions of degradation of the polymeric matrix (240–550°C).

According to the results of gas-chromatographic analysis, the liquid fraction is free of sulfur-containing organic compounds. 47.6 wt % of sulfur present in the initial resin is removed with the gas fraction trapped in the absorber, and 52.4 wt % remains in the solid residue.

The results of the analyses showed that in the gaseous products sulfur is present in the form of SO_2. Comparison of the amounts of oxygen and sulfur distributed among fractions shows that 0.93 wt % of sulfur in the solid residue is not incorporated in functional groups (so-called inactive sulfur [6]). It is known that inactive sulfur may be involved in intramolecular bonds of aromatic rings, sulfone bridges [7], and sulfo esters [8, 9]. This fact indicates that, in a nitrogen atmosphere, thermal desulfurization consists in hydrolytic elimination of sulfo groups, followed by the reaction of the forming sulfuric acid with reducing groups of the resins, with the release of sulfur dioxide. This conclusion is consistent with published data [6]. As we used a flow-type reactor, the released organic substances did not react with sulfur-containing gases, as indicated by the absence of organosulfur compounds in the off-gases.

Granules of the spent cation exchanger after the heat treatment mainly preserve the initial spherical shape. This may be due to appearance of sulfo groups in the m-position in the course of heat treatment and enhancement of cross-linking via phenyl rings [6], or to additional sulfonation of aromatic rings with sulfuric acid [6], i.e., condensation and cross-linking are observed.

The sorption properties of solid residues from pyrolysis of spent ion exchangers are given in Table 1.

The liquid phase formed by heat treatment of the spent anion exchanger consists of two immiscible liquids differing in the density (1.0 and 0.8 g cm^{-3}). At 350 ± 5°C, only the condensate with a density of 1.0 g cm^{-3} is formed. Gas chromatographic analysis showed that the substances mainly removed from the polymeric matrix at this temperature are nitrogen-containing compounds (26.9 wt % dimethylamine and 30.5 wt % trimethylamine; counting on the initial anion exchanger, 7.3 and 8.2 wt %, respectively) and water. The major part of di- and trimethylamine is condensed in the condenser, and the uncondensed fraction (6.2 wt % counting on the initial anion exchanger) is sorbed by water in the absorber.

The thermal degradation products released from the anion exchanger in the temperature range 350–550°C are mainly aromatic compounds containing no nitrogen atoms.

Elemental analysis shows that, upon heat treatment of the spent anion exchanger at 550 ± 5°C, 8.1 wt % of nitrogen (based on the initial amount) remains in the solid residue. The process is accompanied by sintering and breakdown of granules, suggesting the occurrence of degradation and a decrease in the degree of cross-linking of the polymeric matrix.

The content of heteroatoms in the solid residue after heat treatment of spent ion exchangers is plotted in Fig. 3 vs. the process temperature. Distribution of heteroatoms among products of heat treatment at 550 ± 5°C is shown in Fig. 4.

CONCLUSIONS

(1) Heat treatment of spent synthetic ion exchangers AV-17 and KU-2 at 50–550°C was performed.

(2) The degree of deamination of the spent anion exchanger is higher than the degree of desulfonation of the spent cation exchanger.

(3) Liquid fractions of the density about 1.0 g cm^{-3} for the cation exchanger and 0.8 g cm^{-3} for the anion exchanger consist of aromatic compounds free of heteroatoms.

(4) The prospects for using the liquid and solid products of heat treatment of the spent resins as inert fillers, chemical raw materials, and fuel additives are discussed.

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