

DISTRIBUTION OF POTASSIUM DURING PARTIAL NEUTRALIZATION OF ION EXCHANGE CATALYSTS

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The distribution of potassium in partially neutralized cation exchangers was studied by electron microprobe. In the cation exchanger crosslinked with 25% divinylbenzene, potassium is distributed regularly within the entire mass of the grain whereas in the exchanger crosslinked with 50% divinylbenzene, only its 30–40 μm -thin surface layer is neutralized regularly.

In our laboratory we have been concerning ourselves for several years with the study of properties of organic ion exchangers as catalysts for reactions proceeding in the gaseous phase. One of means which we have been trying to employ for this purpose, was a controlled variation of concentration of active centres by partial neutralization of cation exchanger functional groups by alkali ions in an aqueous medium^{1,2}. However, we have not been able to verify directly whether the neutralization is regular in the whole volume of the ion exchanger, *i.e.* whether the fraction of neutralized functional groups on the geometric surface of a particle accessible for reactants from the gaseous phase is identical with that inside the exchanger gel, *i.e.* of groups most probably inaccessible from the gaseous phase. From existing literature data³ it was possible to assume that after a sufficiently long period of contact between the exchanger and the solution of the base, equilibrium concentrations would be reached and the degree of neutralization in the whole volume of the grain would be the same. To verify this hypothesis directly, we had decided to employ electron microprobe. This device makes it possible to perform the elementary analysis on an area of the diameter not greater than 2 μm , so that we were able to determine the distribution of an alkali metal in the section of the ion exchanger grain.

EXPERIMENTAL

In our experiments we used a standard nonporous highly-crosslinked styrene-divinylbenzene sulphonated cation exchanger containing 25 or 50% divinylbenzene. The basic copolymer was a product of the Research Institute of Synthetic Resins and Lacquers, Pardubice, and in our laboratory it was sulphonated by 96% sulphuric acid in 1,2-dichloroethane as swelling agent. This method of sulphonation has been proved to be the best from the point of view of a regular

distribution of sulpho groups in the polymer material⁴. In spite of this — as it will be shown later on — the sulphonation has not been quite regular, which had to be taken into account in evaluating the results. Prepared cation exchangers were washed with 0.5M-KOH, a 10% solution of HCl and finally with distilled water to neutral reaction. They were then contacted with 0.25M-KOH in an amount corresponding to neutralization of 20 or 40% of exchange groups, allowed to stand for 24 h, washed with distilled water and dried. Selected grains of the diameter of 0.3–0.6 mm were embedded into a polyester resin and ground into a plane passing through the grain centre. Before the measurement, an electrically conductive layer was produced on the surface of the samples by vacuum evaporation of carbon. The measurements were performed on a JXA-50A (Jeol) apparatus, which made it possible to follow simultaneously the concentration of both potassium and sulphur, so that irregularities in the distribution of acid groups might be eliminated.

RESULTS

The ratio of concentrations of sulphur and potassium in the ion exchanger crosslinked with 25% divinylbenzene is constant within 10% in the entire grain section (Fig. 1). Absolute concentrations of both elements decrease from the boundary towards the grain centre; this is probably due to irregular sulphonation of the resin. In the highly crosslinked exchanger containing 50% divinylbenzene (Fig. 2), the constant degree of neutralization with a hydroxide solution might produce some irregularities in the potassium distribution only in ion exchangers with an extremely

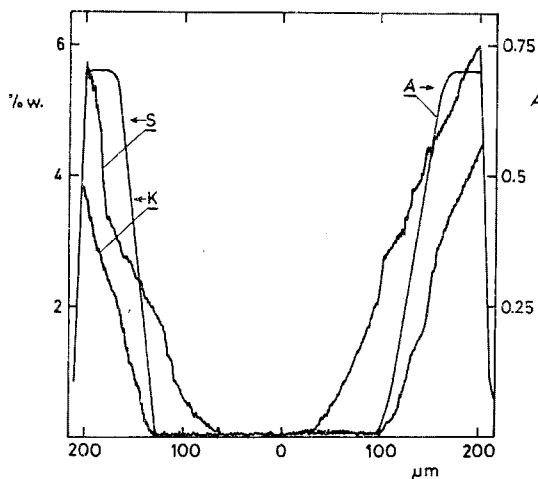


FIG. 1

The Distribution of Sulphur and Potassium Concentrations within a Grain of the Sulphonated Cation Exchanger Crosslinked with 25% Divinylbenzene and Neutralized to 40% with Aqueous Solution of Potassium Hydroxide

A Ratio of wt.% of potassium and sulphur. The zero denotes the grain centre.

TABLE I

Dimensions of Microbeads, which Form Particles of Macroreticular Ion Exchangers, as Calculated from Specific Surfaces Determined by the BET Method

The calculation was performed with the density of the polymeric material equal to 1.4 g/cm^3 .

| Content of divinylbenzene % | Specific surface m^2/g | Mean radius of the microbeads μm |
|--------------------------------|---|---|
| 10 | 3.2 | 0.67 |
| 15 | 33 | 0.065 |
| 25 | 44 | 0.049 |
| 40 | 120 | 0.018 |
| 60 | 230 | 0.009 |

high degree of crosslinking. Most commonly are in use ion exchangers crosslinked with 2–16% divinylbenzene, for which still better conditions for a regular distribution of potassium might be expected.

In our kinetic studies we have been more often using ion exchangers of the macroreticular type as model catalysts. Their texture might be visualized as a cluster

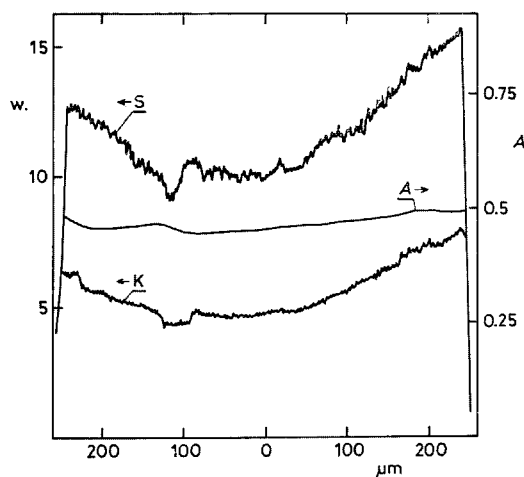


FIG. 2

The Distribution of Sulphur and Potassium Concentrations within a Grain of the Sulphated Cation Exchanger Crosslinked with 50% Divinylbenzene and Neutralized to 40% with Aqueous Solution of Potassium Hydroxide

of microbeads^{5,6} whose mean radius can be calculated from the specific surface of the ion exchanger and density of the polymer material (Table I). It may be seen that dimensions of microbeads which make up the macroreticular ion exchangers are by several orders lower than the thickness of the surface of the polymeric material (30–40 μm) in which the degree of neutralization is regular also for a highly crosslinked ion exchanger. In partially neutralized porous ion exchangers, the concentration of acid sulpho-groups inside the polymeric material will be therefore equal to that on the surface. This justifies the use of data on the degree of neutralization obtained by titration for correlating experimental data on heterogeneous catalysis in the gaseous phase^{1,2}.

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