STUDY OF THE MECHANISM OF ADSORPTION OF Mn$^{2+}$ IONS ON $\gamma$-ALUMINA BY ESR SPECTROSCOPY*

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The ESR technique was used to investigate the sorption of Mn$^{2+}$ on $\gamma$-alumina from aqueous solutions. The results suggest that Mn$^{2+}$ is adsorbed in two main forms: 1) a limited amount ($\sim$10$^{-6}$ mol/g of $\gamma$-alumina) is irreversibly adsorbed on lattice defects, and 2) beyond this amount, Mn$^{2+}$ is reversibly adsorbed as a hydrated complex dispersed on the surface. Upon thermal treatment in air the adsorbed surface species are oxidized while the lattice sites remain unchanged.

Transition metal ions supported on oxide matrices are of great industrial importance as catalysts for many reactions. The manganese (II) ion, because of its easily understandable features, was often used in adsorption studies/1-4/. The aim of the present work was to study the mechanism of adsorption of Mn$^{2+}$ ions on $\gamma$-alumina and the nature of the species formed.

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EXPERIMENTAL

Ketjenfine "Grade E" γ-alumina (surface area 128 m²/g, pore volume 0.54 ml/g) was used in all sample preparations. γ-Alumina dried over P₂O₅ in vacuum was impregnated with aqueous manganese (II) nitrate (Merck) added in quantities equal to the pore volume. Different Mn²⁺ contents of the samples were obtained by changing the solution concentration.

The wet samples were stored over a saturated Ca(NO₃)₂ solution in a desiccator. Successive dehydration was carried out by degassing the samples periodically at room temperature. Part of the dried samples was further fired at 450°C for 2 hrs.

ESR spectra were recorded at room temperature on a Varian V-4502 spectrometer.

RESULTS AND DISCUSSION

γ-Alumina samples stored in a humid atmosphere, in spite of their dry appearance, show manganese ESR patterns (top spectrum in Fig.1), which differs only slightly from the corresponding solution spectrum of the mother liquor used for impregnation. The spectral features of these adsorbed species have been thoroughly investigated /5-6/. They undoubtedly show that a) the manganese(II) ions are still solvated and free to move in capillary-condensed water, and b) they interact only weakly with the solid substrate.

The successive steps of dehydration and adsorption on the alumina surface can be followed by ESR spectral changes (Fig.1). The liquid type spectrum (a) shows increasing broadening with increasing evaporation of water in vacuum (evaporation at 110°C gives the same results). The spectrum of the partially desiccated sample (Fig.1 b) appears as a complex pattern. Its shape is complicated by crystal-field anisotropies due to stronger ion-substrate interactions. Partial immobilization of the hydrated complexes at the liquid-solid interphase because of the different de-