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THE ROLE OF SURFACE CHLORIDE IN THE REACTIONS OF CHLOROFLUOROETHANES ON FLUORINATED CHROMIA CATALYSTS

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The behaviour of chlorofluoroethanes on chromia catalysts, previously treated with HF or H¹⁸F, has been interpreted on the basis of a series of F-for-Cl and Cl-for-F halogen exchange reactions which occur at the catalyst surface. Three types of surface fluoride species are present, only one of which is catalytically active (J. Kijowski, G. Webb and J.M. Winfield, J. Fluorine Chem., 24, 1984, 133 ; 27, 1985, 213). The role of surface chloride in these reactions has now been studied using ³⁶Cl as a radiotracer. Uptake of ³⁶Cl by the fluorinated catalyst is observed by passage of H³⁶Cl at 350°C. It is considerably smaller than uptake of ¹⁸F using H¹⁸F under identical conditions, and increases with increasing temperature in contrast to the situation with H¹⁸F. Approximately 85% of the ³⁶Cl activity is removed by subsequent passage of CClF₂CClF₂ at ≥ 350°C, [³⁶Cl]-labelled CCl₂FCClF₂ being one of the products. Cl-for-F exchange like its F-for-Cl counterpart is therefore a true surface reaction. The remainder of the ³⁶Cl on the catalyst is unaffected even after multiple reactions, and it is suggested that it is directly bound to Cr^{III}. Experiments using mixed HF, HCl, C₂Cl₃F₃ gas flows suggest that HCl has a mild deactivating effect on the fluorination reactions.