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DYNAMIC BEHAVIOUR OF CHLOROFLUOROETHANES AT HALOGENATED SURFACES

M. McGeough, J. Thomson, G. Webb, J. M. Winfield

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ (U.K.)

D. G. McBeth, A. McCulloch and N. Winterton

Research and Technology Department, ICI C and P Ltd., Runcorn WA7 4QD (U.K.)

Apparent dismutation and isomerization reactions of chlorofluoroethanes, occurring at 350 - 425°C over a fluorinated chromia surface, can be accounted for by a halogen exchange model consisting of inter-related F-for-Cl and Cl-for-F reactions [1]. Reactions at other halogenated surfaces are now reported. Isomerization of $\text{CCl}_2\text{FCClF}_2$ at aluminium(III) chloride has been demonstrated previously [2]; it is the major process at room temperature although retention of $\text{CCl}_2\text{FCClF}_2$ at the surface is also significant (25%). A more active surface is produced by pretreatment of AlCl_3 with CH_3CCl_3 . This leads to formation of a purple polymer derived from the dehydrochlorination product $\text{CH}_2 = \text{CCl}_2$ [3]. At this surface, retention of $\text{CCl}_2\text{FCClF}_2$ is less marked (7%) and the major component (93%) of the volatile mixture is CCl_3CF_3 . No detectable [^{36}Cl]-surface activity results when [^{36}Cl]- $\text{CCl}_2\text{FCClF}_2$ is used, suggesting that isomerization may be intramolecular as has been proposed for $\text{CCl}_2\text{FCClF}_2$ at AlCl_3 [2]. Treatment of AlCl_3 with $\text{CCl}_2\text{FCClF}_2$ followed by CH_3CCl_3 results not only in dehydrochlorination of the latter, but also in the liberation of CCl_3CF_3 from the surface. In contrast the almost complete (81%) retention of $\text{CCl}_2\text{FCClF}_2$ by chlorinated γ -alumina blocks any catalytic activity towards dehydrochlorination of CH_3CCl_3 .

- 1 L. Rowley, G. Webb, J.M. Winfield and A. McCulloch, Appl.Catal., in press.
- 2 W.T. Miller, E.W. Fager and P.H. Griswald, J. Am. Chem. Soc., **72**, 705 (1950).
- 3 D.G. McBeth, J.M. Winfield, B.W. Cook and N. Winterton, submitted to J. Chem. Soc. Dalton Trans.