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FLUORINE ION SUPPORTED ON γ -ALUMINA: CHARACTERISATION AND CATALYTIC ACTIVITY

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Alkali metal fluorides, CsF or KF, supported on γ -alumina behave as strong bases under heterogeneous conditions and at low metal fluoride loadings, have catalytic properties [1]. We have extended the physical examination of these materials reported previously [1] to include a radio-tracer study of surface behaviour using ^{35}S - and ^{18}F -labelled SF_4 , SOF_2 , SO_2 and HF as probe molecules. Radiotracer and spectroscopic results indicate the presence of weakly adsorbed SF_4 and SO_2 and permanently retained SF_5^- and SO_2F^- species, surface activity being at a maximum near $5 \text{ mmol MF (g alumina)}^{-1}$. In agreement with previous studies [1] we find that spectroscopic, e.g. i.r., ^{27}Al MAS n.m.r., and structural properties, XRD, of these materials depend on their composition. Transmission electron microscopy is particularly useful; below $5 \text{ mmol MF (g alumina)}^{-1}$ KF particles are detected while at higher loadings formation of Al - F phases becomes progressively more important. Terminal hydroxyl groups present on the surface can be removed by treatment with SF_4 at room temperature. The resulting materials, CsF or KF supported on fluorinated γ -alumina, are efficient catalysts for chlorofluorination of SF_4 by ClF. Catalytic activity is at a maximum ca. $5 \text{ mmol MF (g alumina)}^{-1}$ and poisoning by ClF appears to be less important than is the case for unsupported CsF [2].

- 1 T. Ando, S.J. Brown, J.H. Clark, D.G. Cork, T. Hanafusa, J. Ichihara, J.M. Miller and M.S. Robertson, J. Chem. Soc., Perkin Trans. II, 1133 (1986)
- 2 G.A. Kolta, G. Webb and J.M. Winfield, Appl. Catal., **2**, 257 (1982).