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PRELIMINARY NOTE

Alkali Metal Fluorides Supported on Fluorinated γ-Alumina, Lewis Base and Catalytic Properties

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SUMMARY

Caesium and potassium fluorides supported on fluorinated γ-alumina are active catalysts for the room temperature chlorofluorination of sulphur tetrafluoride by chlorine monofluoride. Maximum catalytic activity is observed at the composition 5.5 mmol g^{-1} in agreement with their behaviour towards volatile Lewis acids.

Caesium and potassium fluorides supported on aluminas are strong bases under heterogeneous conditions. At low composition, below 10 mmol of alkali metal fluoride per g of alumina, they behave as strongly basic catalysts, for example in the Michael reaction; their catalytic activity is greatest near the composition 5 mmol g^{-1}. The basic properties of these materials have been ascribed to surface fluoride anion and to hydroxide groups [1]. The latter can lead to unwanted side reactions and in this communication we show that they can be

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removed by fluorination of the surface without loss in basic or catalytic properties.

The B.E.T. areas of caesium and potassium fluorides supported on γ-alumina (Degussa C) decrease with increasing composition, for example the B.E.T. area of supported CsF is 124-135 m^2g^{-1} (95% confidence limits) at the composition 1.1 mmol g^{-1} and 11-18 m^2g^{-1} at the composition 20.0 mmol g^{-1}. Corresponding values for supported KF are slightly greater. The B.E.T. area of γ-alumina, calcined at 523 K, is 156-172 m^2g^{-1}.

Adsorption of the Lewis acids SF_4, OSF_2, SO_2, OCF_2 and CO_2 on γ-alumina-supported CsF and KF occurs at room temperature as shown by radiotracer experiments using [^{35}S]- sulphur and [^{14}C]-carbon labelled compounds. The greatest surface count rates and thus the maximum extents of adsorption [2,3] occur at the composition 5.5 mmol g^{-1} in all cases. The 'volcano' relationship between surface count rate and composition is illustrated by the behaviour of $^{35}SF_4$ on supported CsF and KF in Fig. 1.

In all cases desorption of the major surface species is rapid on evacuation at room temperature but i.r. spectroscopy shows that the anions SF_5^-, FSO_2^- and F_3CO^- [4] are formed as minor species on the surface and are permanently retained. Similar behaviour occurs on unsupported CsF [5]. The reactions of SF_4, OSF_2 and F_2CO with the surface also involve hydrolysis, since OSF_2, SO_2 and CO_2 are evolved. Hydrolysis is dominant when the supported metal fluorides are prepared by impregnation from aqueous solution followed by calcination at 523 K [1]. It is less marked for supported metal fluorides prepared by impregnation of calcined γ-alumina with caesium or potassium heptafluoroisopropoxides [6] in acetonitrile followed by thermal

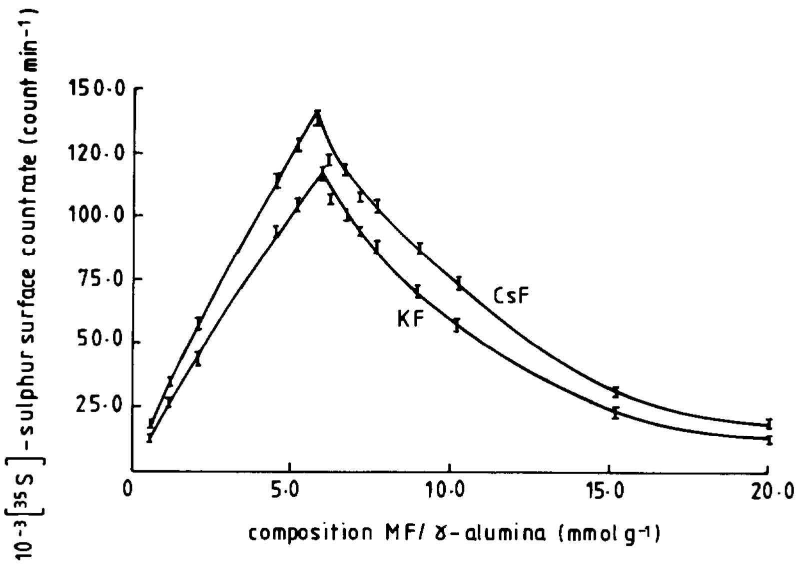

Fig. 1. Variation of the [^{35}S]-sulphur surface count rates with composition for $^{35}SF_4$ + CsF or KF supported on γ-alumina. Initial pressure of SF_4 = 300 Torr.

decomposition and calcination at 523 K, but is still an important reaction.

Surface hydroxyl groups and water adsorbed on the surface are completely removed by exhaustive fluorination, nominally at room temperature, using SF_4 or F_2SO or the combination SO_2 then anhydrous HF. In each case the fluorination process is followed by calcination at 523 K in order to decompose the F^- ion -----SF_4 or ----SO_2 complexes that are formed. Anhydrous HF alone is ineffective since the HF_2^- formed on the surface is not so readily decomposed. Fluorination of the supported metal fluorides results in a reduction in B.E.T. area which is particularly marked at low compositions, for example at the composition 1.1 mmol g^{-1} the B.E.T. area of CsF supported on fluorinated γ-alumina is 32-36 m^2g^{-1}. The adsorption-desorption behaviour of $^{35}SF_4$ on the fluorinated materials however, is very similar to that on the hydroxylated materials but as there is no hydrolysis, the sole, retained species is SF_5^-. The behaviour of $[^{36}Cl]$-chlorine labelled chlorine monofluoride is identical to that shown in Fig 1, the maximum ^{36}Cl surface count rates being observed at the composition 5.5 mmol g^{-1}.

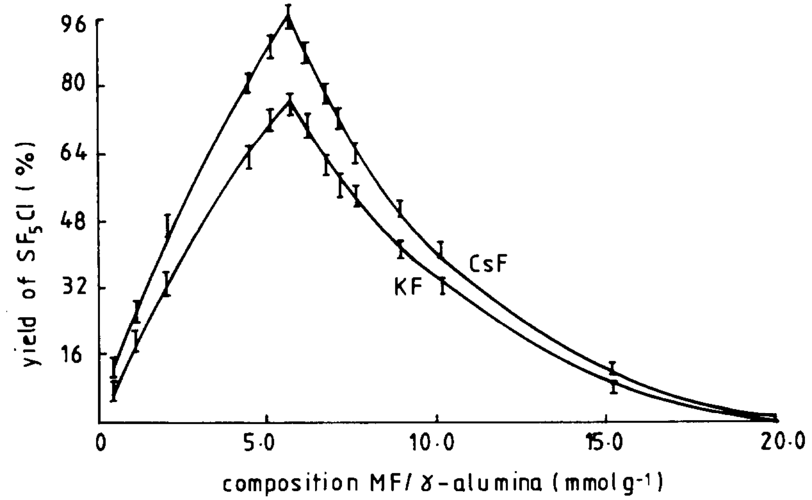

Fig. 2. Variation of the yield of SF_5Cl with catalyst composition. Conditions: 1:1 mole ratio, 5-10 mmol scale, 1 h, room temperature. Yields were constant over 6 runs for a given catalyst sample (2.0 g).

The catalytic ability of the metal fluorides supported on fluorinated γ-alumina was tested using the model reaction $SF_4 + ClF \longrightarrow SF_5Cl$ at room temperature. The variation of catalytic ability with composition, as determined by the yield of SF_5Cl, is shown in Fig.2, maximum yields being obtained at 5.5 mmol g^{-1}.

Kinetic studies using 1:1 mole ratios of ^{36}ClF : SF_4 and ClF : $^{35}SF_4$ are consistent with a mechanism identical to that proposed previously for unsupported CsF [3]. The second order rate constants determined from the decrease in ^{36}Cl or ^{35}S surface count rates with time vary with catalyst composition in a manner very similar to that shown in Fig. 2.

The striking resemblance between Fig.1 and Fig.2 indicates the existence of a basic site that is common to both hydroxylated and fluorinated surfaces and all the evidence points to the direct involvement of F^- anion.

Transmission electron microscopy and electron diffraction examination of KF supported on γ-alumina over the composition range 0.2 to 8.8 mmol g^{-1} shows that at compositions < 5.5 mmol g^{-1} KF particles are present. Particle sizes are ca. 25, 33 and 40 Å respectively for the compositions 2.0, 4.4 and 5.5 mmol g^{-1}. The particles are well dispersed but KF is mobile under the influence of the electron beam and quite large crystals are formed. Particles of KF are present also at 4.4 mmol g^{-1} on a support which has been fluorinated with SF_4. Below 5.5 mmol g^{-1} there is no evidence for the formation of AlF_3 or simple fluoroaluminates but at 8.8 mmol g^{-1} and above, M_3AlF_6, M = Cs or K, are present as shown by X-ray diffraction and in agreement with previous work [1].

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