

RADIOTRACERS IN FLUORINE CHEMISTRY. PART VI. SURFACE
AREAS OF IONIC METAL FLUORIDES. EFFECT OF PRETREATMENT

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SUMMARY

Determination of CsF, TlF, and RbF surface areas by the B.E.T. method using ^{85}Kr is described. Surface areas of CsF and TlF samples are increased markedly by sample pretreatment, either by heating in vacuo or by reaction with hexafluoroacetone in acetonitrile. The latter method is particularly effective for CsF. RbF samples are less sensitive to pretreatment.

INTRODUCTION

Ionic, metal fluorides are widely used under heterogeneous conditions. A complete understanding of their behaviour requires a knowledge of their surface areas, including the effect on surface area of sample pretreatment. This aspect of ionic fluoride chemistry has received little attention, although for some metal fluorides there appears to be a correlation between surface area and ability to undergo 18-fluorine exchange with labelled sulphur tetrafluoride or carbonyl fluoride [1]. We now report the effect of sample pretreatment on the surface areas of caesium fluoride, a widely used catalyst [2], rubidium fluoride, an alternative to CsF in some reactions [3,1], and thallium(I) fluoride which

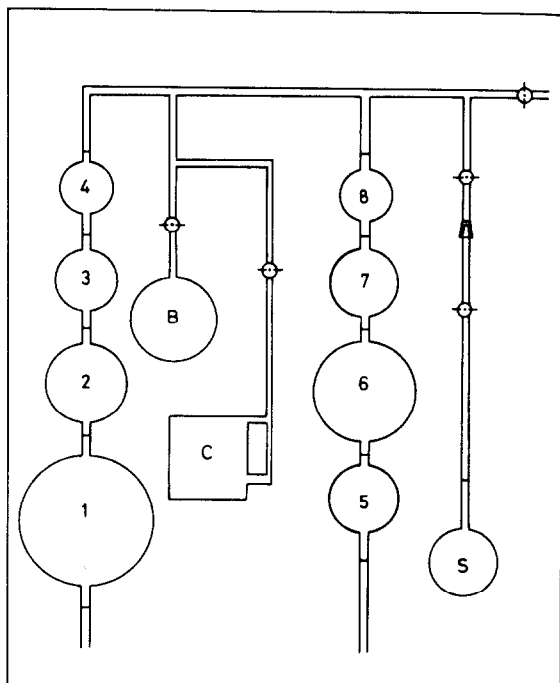
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has no catalytic activity, at least in the reaction $\text{SF}_4 + \text{ClF} \rightarrow \text{SClF}_5$ [1]. Experimental aspects of the method used for measuring small surface areas ($< 1 \text{ m}^2 \text{ g}^{-1}$) are described.

EXPERIMENTAL

Surface area determination

Surface areas were determined by the B.E.T. method using the radio-isotope 85-krypton as adsorbate. The advantage of using radioactive gas is that small changes in pressure can be determined relatively rapidly and with a high precision. The apparatus, evacuable to $\leq 10^{-5}$ torr, was similar to that described by Aylmore and Jepson [4], modified to facilitate the handling of hygroscopic solids. It is shown schematically in the Figure.



FIGURE

B.E.T. apparatus.
Volumes of the
various sections
were as follows:

bulb 1,	63.07 cm^3
2,	29.53 cm^3
3,	8.79 cm^3
4,	5.19 cm^3
5,	17.18 cm^3
6,	42.39 cm^3
7,	10.90 cm^3
8,	6.32 cm^3
S,	8.97 cm^3
C,	50.08 cm^3

The calibrated system constructed from Pyrex glass, consisted of two sets of bulbs, 1 - 4 and 5 - 8, each with a mercury reservoir, a ^{85}Kr storage bulb (B), a thin-walled counting vessel (C) and the adsorbent sample bulb (S). The manifold was also connected to reservoirs containing ^{85}Kr (Radiochemical Centre, Amersham) and non-radioactive Kr (BOC Ltd.), and to a trap containing charcoal activated at 578 K in vacuo. Diluted ^{85}Kr was prepared in the latter, to give a working activity of ca. 10^3 counts/sec/torr, and was equilibrated at 77 K overnight before use.

A calibration curve of ^{85}Kr activity against pressure was determined over the pressure range 0.09 - 0.29 torr. Pressures were measured using a Pirani gauge and ^{85}Kr activities determined using a Geiger-Muller counter (Mullard ZP 1481) externally mounted immediately below the counting vessel (C). Approximately 0.5 h. was required for equilibrium to be attained after each pressure change. The count rates were reproducible, the time of counting being adjusted to give a total count of $\geq 10^4$, to minimise counting errors. The calibration was checked at regular intervals and was re-determined for each fresh sample of diluted krypton.

The sample bulb (S) was loaded with an accurately weighed sample (~ 0.5 g) of metal fluoride in a glove box, and was then outgassed for several hours. Bulbs 1 - 8 were filled with mercury and ^{85}Kr admitted to the manifold from (B) to a pressure less than the S.V.P. of Kr at 77 K. The relation between ^{85}Kr activity and volume, and hence between pressure (P torr) and volume ($V \text{ cm}^3$) at room temperature (T K) was determined, the final measurement corresponding to 1 - 8 empty. A plot of V vs. T/P was linear with a negative intercept on the V axis corresponding to the dead space + sample bulb volume ($57.16 + 8.97 \text{ cm}^3$). Since adsorption isotherms were obtained with (S) held at 77 K, the corrected V vs. T/P plot was a line parallel to the experimental line with an intercept of $-(57.16 + 8.97.T/77)$. This was confirmed in a separate experiment.

Bulb (S) was immersed in liquid N_2 , the level being kept constant, and a second V vs. T/P relationship determined.

For samples of surface area $< 0.1 \text{ m}^2 \text{ g}^{-1}$ bulbs 1 - 4 were used, 5 - 8 being filled with mercury before the run was commenced. The slope of this isotherm was less than that of the corrected 'room temperature' isotherm, the differences in $V(\Delta V \text{ cm}^3)$ at given T/P values being the volumes of Kr adsorbed. The number of molecules adsorbed (x) was $(P\Delta V/77)(N/R)(1/760 \times 10^{-3})$, where $N \text{ mol}^{-1}$ = Avogadro number and $R \text{ l at mol}^{-1} \text{ K}^{-1}$ = the gas constant. The slope of the linear B.E.T. plot $P/x(P_0 - P)$ vs. P/P_0 was $1/x_M$, where P_0 = S.V.P. of Kr at 77 K (0.62 torr) and x_M = number of Kr molecules required to form a monolayer. The surface area = $x_M \cdot 19.5 \times 10^{-20} / (\text{wt. of sample}) \text{ m}^2 \text{ g}^{-1}$, where $19.5 \times 10^{-20} \text{ m}^2$ = the Kr molecular area. The overall error on the surface areas was $\pm 0.02 \text{ m}^2 \text{ g}^{-1}$, the major source of error being graphical.

Sample preparation

CsF and RbF (B.D.H. Optran grade) and TlF (Alfa Inorganics 99%) were stored and manipulated in a glove box equipped with Ar or N_2 recirculation and purification (Lintott Engineering Co.). They were thoroughly ground using an agate pestle and mortar before use. Three pretreatment methods were used as follows:

- (1) A sample contained in a stainless steel vessel was heated at 423 K in vacuo for 24 h. After cooling it was reground. This procedure was repeated once or twice when longer pretreatment times were required.
- (2) A sample contained in a Ni boat was heated at 573 K or 773 K in a dry N_2 flow for 2 h. After cooling in N_2 it was reground.
- (3) A sample ($\sim 2 \text{ g}$) was shaken for 24 h, at room temperature in a stainless steel vessel containing several stainless steel ball bearings with a mixture of acetonitrile (5 ml), dried by multiple refluxes over CaH_2 then P_2O_5 followed by storage in vacuo over activated 4A molecular sieves, and hexafluoroacetone (Fluorochem), purified by low temperature, trap-to-trap distillation in vacuo, sufficient to produce an

autogeneous pressure of ca. 7 at. Volatile material was removed, the vessel was heated at 373 K under dynamic vacuum for 10 h. to decompose any adduct formed [5], and pumped overnight at room temperature, after which the sample was reground.

RESULTS AND DISCUSSION

CsF and RbF have the rock salt structure, while TlF exists as a distorted form of this structure at room temperature, the presence of aspherical Tl^+ cations being implied [6]. Surface areas of these fluorides, pretreated in various ways, are given in the Table.

TABLE

Surface areas of metal fluorides

Pretreatment method	Surface area ($m^2 g^{-1}$) (a)		
	CsF	TlF	RbF
None	0.04 0.04	0.11 0.13	0.04 0.03
423 K, 24 h, vacuo	0.09 0.09	0.34 0.37	0.04 0.04
423 K, 48 h, vacuo ^(b)	0.18 0.19	0.35 0.37	0.04 0.05
423 K, 72 h, vacuo ^(b)	0.18 0.20	0.36 0.37	(c)
573 K, 2 h, N_2	0.08 0.08	0.18 0.18	(c)
773 K, 2 h, N_2	0.06 0.07	(c)	(c)
$(CF_3)_2CO$ + MeCN then 373 K, 10 h, vacuo	0.37 0.41	0.34 0.35	0.08 0.09

(a) Determined on different samples. Error $\pm 0.02 m^2 g^{-1}$.

(b) Two or three periods of 24 h; reground after each period.

(c) Not studied.

Heating in vacuo, reaction with $(CF_3)_2CO$, or fusion followed by grinding, are commonly used methods for activating CsF prior to its use as a catalyst [2, 3, 7, 8].

The surface areas are small and those of untreated CsF and RbF must be determined essentially by geometric factors. The fluorides studied are off-white after thermal pretreatment but otherwise are unchanged in appearance. Heating in vacuo at 423 K produces significant increases in the surface areas of CsF and TlF, the limiting periods for pretreatment being 48 h for CsF and 24 h. for TlF. The latter compound undergoes a phase change at 356 K and this may be partly responsible for the increase in surface area. Heating in a N_2 atmosphere at higher temperatures is not so effective in increasing surface areas, although small increases are observed. In the thermal pretreatments the processes involved will be removal of surface adsorbed H_2O , dislocation production, and sintering. The latter will be particularly important for TlF due to its relatively low m.p., 700 K compared with 976 K for CsF and 1048 K for RbF [9]. For both CsF and TlF, sintering appears to be more important when pretreatment is carried out in N_2 . Because of the results obtained, pretreatment by fusion was not studied.

The other method used involves pretreatment with $(CF_3)_2CO$ and MeCN at room temperature, and under these conditions CsF reacts to give $Cs^+OCF(CF_3)_2^-$ [5]. Thermal decomposition of this adduct in vacuo produces CsF which has a porous appearance and a high surface area. Apparently a relatively open bulk solid structure is retained after decomposition of the adduct, and the CsF particle size is decreased. In contrast the surface area of TlF after treatment with $(CF_3)_2CO$ and MeCN is little different from those samples subjected to thermal treatment in vacuo. This suggests that the important step is heating at 373 K rather than reaction between TlF and $(CF_3)_2CO$.

TlF does not form an adduct with F_2CO [7] and as the thermal stabilities of $M^+OCF(R_F)_2^-$ adducts are in the order $R_F = F > CF_3$ [5,7], isolation of $TlOCF(CF_3)_2$ is not likely.

There is disagreement concerning the lattice energy of TlF [6, 10] but it is greater than that of CsF and comparable to those of RbF and KF, for which adduct formation with $(CF_3)_2CO$ has been demonstrated [5]. It appears therefore that TlF does not react with $(CF_3)_2CO$ for kinetic rather than thermodynamic reasons.

The thermal pretreatment methods used have little or no effect on the surface areas of RbF samples and pretreatment with $(CF_3)_2CO$ and MeCN results in only a small increase. Adduct formation therefore does not automatically lead to larger surface areas, and presumably the rates of formation and decomposition of an adduct determine the surface area obtained. The smaller surface area of RbF will be one factor determining the generally poorer catalytic ability of RbF compared with CsF, but comparison between CsF and TlF indicates that surface area is not the sole factor involved.

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