Alumina-supported Fluoride Reagents for Organic Synthesis: Optimisation of Reagent Preparation and Elucidation of the Active Species

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Reagent loading and drying conditions have been compared for alkali metal fluride (MF)–alumina supported reagents, by reaction studies and a series of analytical techniques. The reaction studies indicate that whereas a combination of low MF loadings and highly efficient drying procedures give the best reagents for catalytic reactions, somewhat higher loadings and more moderate drying conditions give the best reagents for non-catalytic reactions. The analytical studies enable some rationalisation of the reaction results as well as providing important clues concerning the nature of the active-basic species. The formation of OH^- on the reagent surface cannot be entirely responsible for the high basicity of the reagents and it seems that co-ordinately unsaturated F^- ions on the reagent surface play an important role in the behaviour of the reagents. High MF loadings and high drying temperatures result in significant structural damage to the reagents with resulting loss in activity.

A diverse range of synthetic reactions have been efficiently accomplished in recent years using fluoride reagents.[1] There has also been a concurrent growth in the use of reagents adsorbed on insoluble inorganic supports[2] for organic synthesis. In previous papers we have reported the enhanced basicity of alkali metal fluorides (MF) supported upon alumina and shown them to be efficient and versatile solid bases for a variety of substitution, elimination, addition, and condensation reactions.[3–6] Several other papers have also highlighted the utility of this convenient solid base and some useful applications of it have been reported.[7] Our studies have suggested that the nature of the reaction and the role of the basic reagent are important factors to consider in determining appropriate MF–alumina preparations. In this paper we present reaction studies and describe analytical investigations on MF–alumina (M = Cs or K) which enable us to compare the optimum reagent preparations for both catalytic and non-catalytic uses. We also discuss the cause of the enhanced basicity.

The aluminas used in our studies are high surface area (*ca.* 125 $m^2\ g^{-1}$) activated γ-aluminas which have a maximum surface hydroxy coverage in the range 3.6—14.5 OH nm^{-2}. These values represent the estimated total number of surface lattice sites considering the alumina surface to be comprised of the (100), (111), and (110) planes of its defect spinel structure.[8] Several studies of surface hydration have shown average OH densities within a range of 8—9 surface hydroxy groups nm^{-2}.[8,9]

On the basis of our previous experience with silica-supported $KMnO_4$,[10] we considered that an evenly dispersed monolayer coverage of MF on the hydroxylated surface of alumina could be obtained if the amount loaded was limited to the average number of surface hydroxy groups. A range of CsF and KF loadings, 0.6—10 mmol MF g^{-1} Al_2O_3, representing surface coverages of 3—50 molecules nm^{-2} (surface F^-:OH ratios of 1:3—6:1), were prepared in order to compare their efficiencies for promoting reactions and to analyse their physical properties. For a catalytic reaction we used the Michael addition of a nitroalkane to an enone acceptor, which has already been shown to be very efficiently catalysed by supported and unsupported MF.[5] The fluoride-promoted *O*-alkylation of phenol was used as a model non-catalytic reaction. We have previously chosen this reaction to compare the effectiveness of several different supports,[3] alkali metal cations, some loading ratios of fluoride to alumina, and reaction solvents.[4] We now report further studies on these catalytic and non-catalytic uses of MF–alumina.

Experimental

The alumina used was Merck 90 neutral, grade 1 for chromatography. MF–Alumina (or KCl–alumina) reagents were prepared as described previously[3–6] by impregnation of MF (or KCl) onto alumina from aqueous solution. Typically, KF (17.4 g) was dissolved in water (*ca.* 400 ml) in a 1 l Buchi flask. Alumina (30 g) was then added and the bulk of water was removed by rotary evaporation at *ca.* 50 °C. Samples were dried under the stated conditions (Tables 1—4, Figures 1, 2, 3, and 5) using either the rotary evaporator or drying pistol for at least 2 h. 'Dry' preparations were made by grinding together the calculated weights of dried MF and Al_2O_3 under a dry nitrogen atmosphere. Deactivated alumina was prepared by washing with water followed by drying at *ca.* 90 °C on a rotary evaporator.

I.r. spectra were recorded on a Perkin-Elmer 683 ratio-recording spectrometer interfaced to a dedicated 64K data station, with samples prepared as KBr discs. *X*-Ray powder diffraction measurements were obtained with either a Debye-Scherer chamber 807 camera (*ca.* 2.5 h exposure) or a Rigaku Denki 4032A2 spectrometer. Thermogravimetric analyses up to 1 000 °C were performed on a Stanton Redcroft T.G. 750 system. Weight losses up to 300 °C were all measured on a Shimadzu DT-40 thermal analyser at 10 °C min^{-1} under dry N_2. Surface areas were measured by the BET method using Argon gas on a Micromeritics High Speed Surface Area Analyser 2205,[11] samples being prepared by degassing with argon for 40 min at 80—90 °C. ^{19}F Solid-state MAS spectra were run on a Bruker CXP200 spectrometer with an operating frequency of 188.23 MHz (all run at ambient temperature).

Gas chromatographs were obtained using either a Pye Unicam 104 or a Shimadzu GC-7A instrument. A 3% Silicone

Table 1. KF Al_2O_3 and KOH Al_2O_3 catalysed Michael addition[a]

Run	Reagent loading mmol KF g^{-1} Al_2O_3	Reagent drying °C/ mmHg		% Yield of 4-nitrohexan-2-one[b] time/s 150	 210	 270
1	0.6	90	20	40.2	61.8	68.8
2	0.6	200	0.1	63.0	67.0	81.2
3	2	90	20		60.0	69.7
4	2	200	0.1	43.5	60.7	71.2
5	2	600	760		57.7	63.7
6	5	90	20	42.6	61.5	77.2
7	5	200	0.1		61.0	70.9
8	10	90	20		65.7	75.5
9	10	200	0.1		15.9	18.8
10	10	600	760			9.4
11	1[c]	90	20	56.4	68.7	73.5
12	1[c]	200	0.1	46.9	59.9	77.9
13	1[c,d]	600	760		76.2	88.9
14	0[e]	90	20			5.8

[a] 0.5 mmol KF (0.25 mmol KOH) used, $EtNO_2$ (0.05 mol) + buten-2-one (2.5 mmol) in acetontrile (5.0 ml). [b] By g.l.c. [c] KOH–Al_2O_3. [d] 0.5 mmol KOH. [e] 0.5 g Al_2O_3.

Table 2. Alkylation of phenol using KF alumina and KOH–alumina

Run	Reagent[a] loading mmol KF g^{-1} Al_2O_3	Reagent[a] drying °C/ mm Hg		% Yield of MeOPh[b] Time/min 90	 300
1	5	90	20	89.8	100
2	5	80	0.1	76.1	99.4
3	5	120	0.1	77.2	98.9
4	5	200	0.1	59.0	84.2
5	5	200	0.1[c]	92.5[d]	
6	5	90	20	94.5[d]	
7	10	90	20	75.1	96.7
8	10	90	20[e]	35.9	62.8
9	10	600	760	10.8	
10	2	90	20	35.5	55.3
11	2	600	760	5.6	
12	1[f]	90	20	25.7	38.9
13	1[f]	200	0.1	14.8	21.7

[a] 2 mmol KF (1 mmol KOH) for the reaction of phenol (0.5 mmol) with MeI (1.6 mmol). [b] Determined by g.l.c. [c] 2.5 mmol H_2O added to reagent before use. [d] % Yield after 110 min. [e] 0.8 g Al_2O_3 added, *cf.* reactivity of 2;90;20 reagent. [f] KOH–alumina samples.

OV1 column was used for the alkylation analysis and a 5% PEG 20M for the Michael addition.

Acetonitrile was dried over 4A molecular sieves. Most other chemicals were untreated laboratory reagents (unless stated otherwise).

Michael Addition of Nitroethane to Buten-2-one.—A solution containing an excess of nitroethane (3.5 ml, 0.05 mol) and buten-2-one (0.2 ml, 2.5 mmol) in dry MeCN (5.0 ml) was shaken with the catalyst (0.5 mmol F^- or 0.25 mmol OH^-) at room temperature. Samples (100 µl) were removed at intervals during 15 sec breaks in the shaking, and rapidly quenched in dichloromethane (2 ml) before being injected into the gas chromatograph. The peak area ratio of the nitroketone adduct to the excess of nitroethane was monitored as a measure of the % reaction. Catalysts typically gave 100% reaction within 10 min.[5]

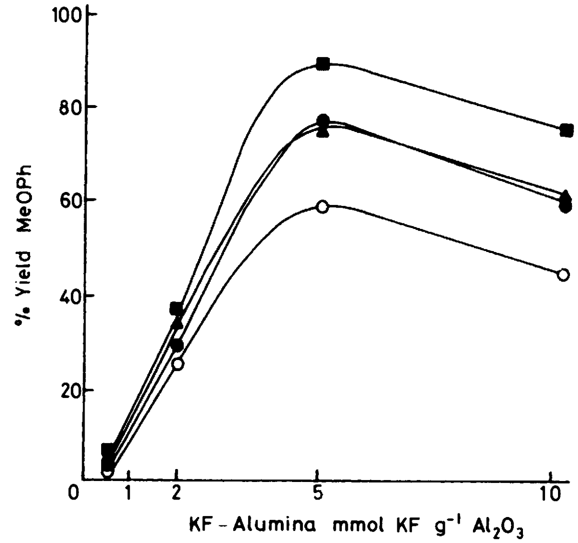

Figure 1. Effects of drying and F^- loading on the activity of KF-alumina in promoting the condensation of PhOH and MeI. ■, 90 °C/20 mmHg; ▲, 80 °C/0.1 mmHg; ● 120 °C/0.1 mmHg; ○, 200 °C/0.1 mmHg

Alkylation of Phenol with Iodomethane.—Phenol (0.94 g, 10 mmol) and dodecane (1.0 ml) were mixed and made up to a 100 ml standard solution in MeCN. MF–Alumina or other catalyst (2 mmol F^-, 1 mmol KOH) was added to the phenol solution (5 ml, 0.5 mmol) and then iodomethane (100 µl, 1.6 mmol) was added. The reaction was either vigorously stirred magnetically (continuously monitored reactions) or shaken in a Teflon-coated screw-cap test tube and the % of methoxybenzene determined by g.l.c. analysis (dodecane internal standard).

Titrimetric Analyses.—The samples of KF–alumina (0.5 g alumina) were shaken for 5 min in water (5.0 ml) or 1.0M aqueous HCl (5.0 ml). The liberated base or the remaining acid was then titrated with standard acid (0.1M aqueous HCl) or base (0.2M aqueous NaOH).

Results and Discussion

Reaction Studies.—The Michael addition of nitroethane to buten-2-one was used as a model system for the study of the relative efficiencies of the supported metal fluorides in a catalytic reaction. Samples of KF–alumina, prepared at a range of loadings and drying conditions, were used and the observed yields of Michael adduct are given in Table 1. It is clear that the very high reagent activity is almost independent of loading and drying conditions over most of the range chosen. However, a small but consistent improvement in reactivity is observed for the lowest loading (*cf.* runs 1, 2) after drying at 200 °C, whereas high-temperature drying of the highest loading (*cf.* runs 8—10) produced the only samples which showed very low catalytic activity. As a comparison, it was noted (runs 11, 12) that KOH–alumina reagents containing 0.25 mmol of base were of similar activity to the KF–alumina reagents containing 0.5 mmol of KF. The supported KOH reagent was also found to retain its catalytic activity after calcination at 600 °C (run 14).

The *O*-methylation of phenol with MeI was promoted using several KF–alumina reagents (fixed ratio of F^- : phenol and excess of MeI) and the % yields of methoxybenzene were determined by g.l.c. after 90 min of reaction (see Table 2 and Figure 1). Reactions assisted by some MF–alumina reagents were monitored throughout (Figure 2), by intermittent sampling of the reaction solutions. The only supported reagents which gave

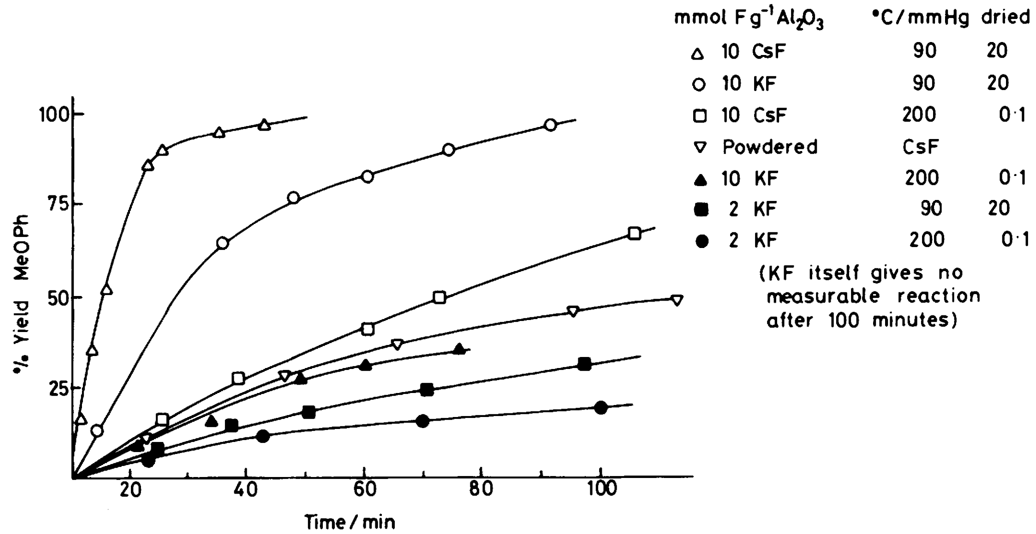

Figure 2. Rate curves for the condensation of PhOH and MeI promoted by F^-

complete conversion were the highly loaded ones (10 mmol MF g^{-1}). Loadings of 2 mmol F^- g^{-1} (1:1 F^-:surface OH^-) and less were found to become ineffective before total conversion. The reagents were also observed to become less active upon drying, as shown in Figure 1 and 2, and by comparing runs 1—4, 7/9, and 10/11 in Table 2.

Interestingly, the activities of the 10 and 2 mmol g^{-1} reagents dried at 90 °C/*ca.* 20 mmHg are similar when sufficient deactivated alumina (see Experimental section) is added to the former to enable equivalent amounts of F^- and alumina to be compared (*cf.* runs 7/8/10, Table 2). Runs 5 and 6 show the important observation that the readdition of water (approximately an equimolar amount of H_2O to F^-) to the highly dried 5 mmol g^{-1} reagent restores its high activity, observed before drying at 200 °C. In order to compare and contrast the activities of F^- and OH^- impregnated on alumina, a 1 mmol g^{-1} loading of KOH–alumina (1 mmol OH^-) was used to promote the alkylation. The supported hydroxide was significantly less effective than fluoride, as shown by comparing runs 10 and 12 (Table 2).

Optimum Reagent Preparations.—The above results show the importance of carefully controlling the loading and drying conditions for obtaining the optimum activities from MF–aluminas. The efficient dispersion and coverage of metal fluoride as well as the quantity of residual water are important factors in determining activity. The optimum reagent preparations do appear to be dependent on the nature of the reaction. Whereas a moderately dried 5 mmol g^{-1} loading of KF is most effective for the methylation of phenol, a lower loading of 0.6 mmol g^{-1}, dried more vigorously, is marginally the best catalyst for the Michael addition of buten-2-one and nitroethane. Certainly the reagent preparation is less critical for the catalytic reaction though, and highly efficient catalysis could be obtained with a wide range of loadings and dryings. This is presumably because only a few active basic sites are sufficient to promote reaction.

Although adsorption of reactants on the support surface may often be considered beneficial in reducing the entropy of activation for MF–alumina promoted reactions, it may prevent or slow reactions if adsorption is strong and not in the vicinity of an active basic site. Thus it was possible to release unchanged phenol from the lower loaded MF–aluminas (< 5 mmol g^{-1}) by the addition of water, after they had become ineffective in promoting further alkylation. The inability of the low-loaded reagents to promote 100% alkylation may also be at least partly due to deposition of a metal iodide by-product. This salt may accumulate in the alumina pore structure during the reaction and begin to block the entry of reactants into the active sites of the MF–alumina reagents.

The reactivation of the highly dried reagents by water (run 5, Table 2) shows the importance of controlled drying and indicates an important role for water in determining the activity of these reagents. The water content of KF–alumina reagents was recently noted to be a critical factor in determining reaction selectivity with them.[7g]

Analytical Investigations.—*Powder X-ray diffraction analyses* were performed on samples of KF–alumina. The monolayer-loaded reagent (2 mmol F^- g^{-1}, sample 1) showed only a diffraction pattern of alumina whereas the high loading (10 mmol F^- g^{-1}, sample 2) showed a clear pattern corresponding to crystalline KF and the presence of K_3AlF_6. This compound may be formed by reaction of F^- with the alumina surface [equation (1)] and it can be seen that hydroxide is also liberated.

$$12KF + 3H_2O + Al_2O_3 \longrightarrow 6KOH + 2K_3AlF_6 \quad (1)$$

A 'dry' preparation of KF–alumina at the high loading ratio 6 F^-:1 OH (sample 3) showed only KF and alumina diffraction patterns, even when ground in non-aqueous solvents (CH_3CN, hexane). Although the amount of KF at 2 mmol g^{-1} loading is only slightly above the lower limit of detection (5—10% w/w) for this technique, the lack of a KF diffraction pattern would seem to suggest that KF is well dispersed and that no large clusters are present in the monolayer coverage.

X-Ray analyses were also performed on the supported reagents recovered after use in promoting the reaction of excess of phenol and iodomethane. Both the 'wet' and 'dry' prepared, highly loaded, reagents showed *X*-ray diffraction patterns of K_3AlF_6 as well as KI and alumina but notably no KF or KHF_2, indicating that the reaction of F^- with the alumina surface may be facilitated by the room-temperature alkylation, which can formally produce HF as a by-product [equations (2)—(4)].

$$PhOH + MeI + KF \longrightarrow PhOMe + KI + HF \quad (2)$$

$$6HF + Al_2O_3 \longrightarrow 3H_2O + 2AlF_3 \quad (3)$$

$$2AlF_3 + 6KF \longrightarrow 2K_3AlF_6 \quad (4)$$

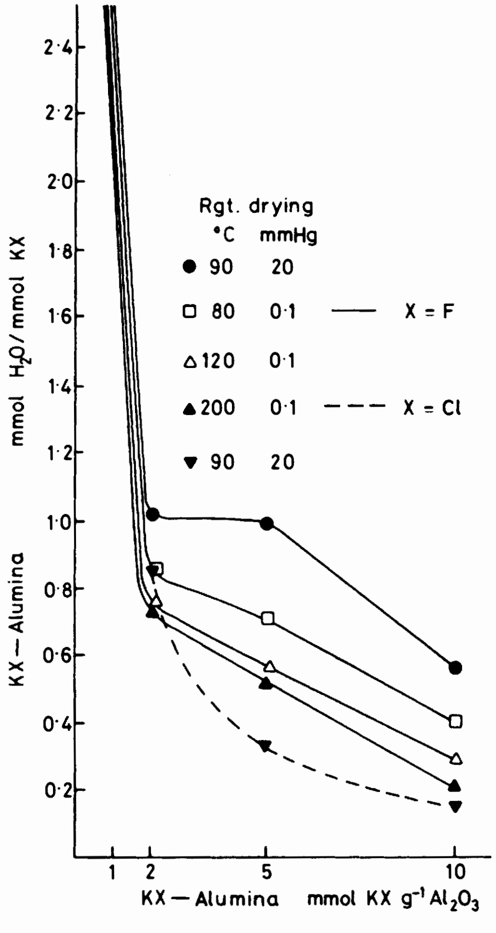

Figure 3. Residual water content in KF–alumina reagents

Thermogravimetric analyses were performed on KF–alumina samples. Samples with loadings of 2 and 10 mmol g^{-1} gave similar results. The major weight loss occurs at 45—100 °C, due to the removal of physisorbed water, and this is then followed by continued slow weight loss up to 500 °C. A second weight loss over the temperature range 500—700 °C may be due to continued surface dehydroxylation, possibly promoted by F^- (fluorodehydroxylation). At temperatures exceeding *ca.* 850 °C a further significant weight loss was observed for all samples when similar quantities of KF were compared. The final weight loss is presumably due to sublimation of KF (m.p. 860 °C) and possibly any K_3AlF_6 (m.p. 1 025 °C) formed.

Weight losses from KF– and KCl–alumina samples (heated to 300 °C) were measured to quantify the amounts of water remaining after employing the different drying conditions for the range of loadings studied. Figure 3 shows the (mmol H_2O)/(mmol KX) *versus* KX loading for the reagents. At low loadings of KF (<2 mmol g^{-1}) the reagents contain large amounts of water relative to KF and they behave as untreated alumina with regards to drying. At loadings above 2 mmol g^{-1} (monolayer coverage) the water content becomes almost directly dependent on the KF loading under each of the drying conditions. One notable exception to this trend is the 5 mmol g^{-1} reagent dried at 90 °C (the most active reagent for the alkylation), which contained relatively more water (1 mmol H_2O/mmol KF) than predicted by the linear relationship with loading (Figure 3). This anomalous behaviour upon moderate drying may well be directly associated with the very high activity of the reagent, which may correspond to a dispersed monohydrate, $KF{\cdot}H_2O$. The KCl–alumina reagents behaved quite differently from the KF–alumina ones and showed drying characteristics similar to untreated alumina.

I.r. analyses were performed on KF–alumina samples of different loadings and degrees of drying. The 2 mmol g^{-1} KF–alumina, recorded after 60, 250, and 1 000 °C heating (Figure 4), shows sharpening and gradual loss of the band at 1 640 cm^{-1}, which is due to the bending mode of physisorbed water. A broad band at 1 410 cm^{-1} similarly sharpened after heating to 1 000 °C to become centred at 1 385 cm^{-1}. Other notable changes are the loss of the absorption at 1 520 cm^{-1} and the decrease in the

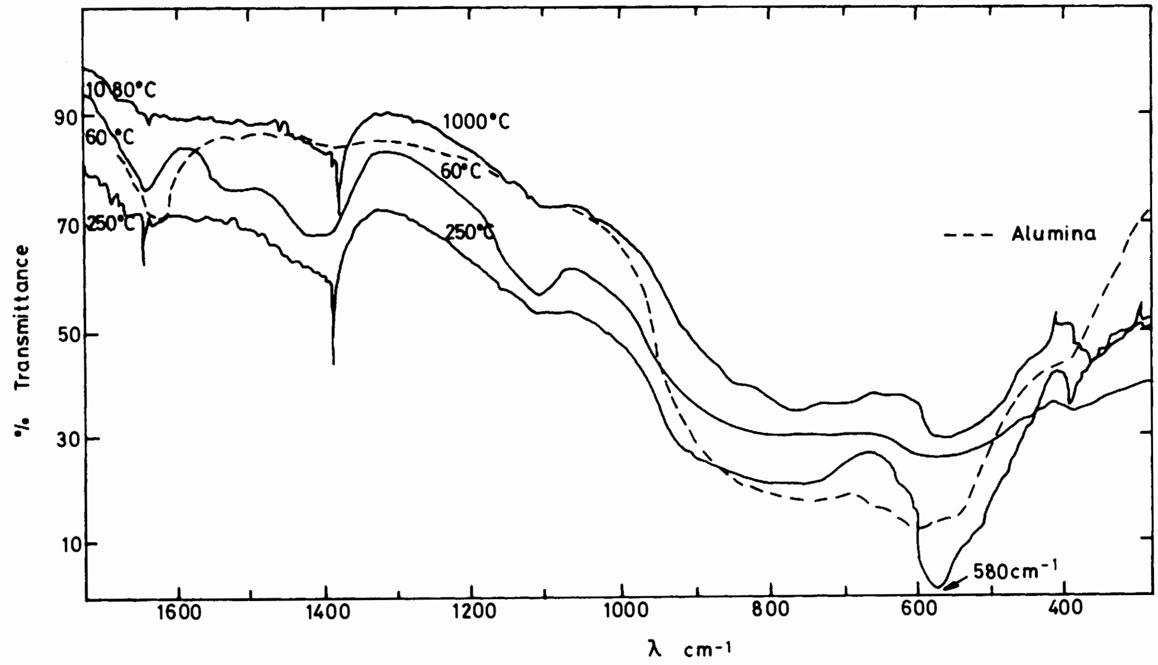

Figure 4. I.r. spectra of KF–alumina (2 mmol g^{-1} Al_2O_3) after heating to 1 000 °C, 250 °C, and 60 °C

Table 3. Titrimetric analysis of KF–alumina basicity

Reagent[a]			A	B	C
mmol KF g^{-1} Al_2O_3	°C/	mmHg	Aqueous wash[b] mmol base/mmol KF	Aqueous acid wash[c] mmol acid neutralised/mmol KF	H_2O-insoluble basicity fraction Δ(B–A)/B
0.6	90	20	0.18	0.69	0.74
2	90	20	0.21	0.81	0.74
5	90	20	0.33	0.84	0.61
10	90	20	0.37	0.62	0.40
2	200	0.1	0.25	0.93	0.73
10	200	0.1	0.40	0.71	0.44
1[d]	90	20	0.68[e]		
1[d]	200	0.1	0.55[e]	0.79	0.30
KF (5 mmol)			0.00	0.03	1.00

[a] Deactivated alumina used as a blank for both aqueous and aqueous acid washes. [b] Each reagent (0.4 g Al_2O_3) shaken with 5 cm^3 H_2O for 5 min. Solutions decanted and two further water washes rapidly done before the combined aqueous wash was titrated with 0.1M aq. HCl to phenolphthalein end point. [c] Samples (0.5 g Al_2O_3) shaken with 5 cm^3 of 1.0M aq. HCl for 5 min. Solutions quickly titrated with 0.2M aq. NaOH to methyl red end point. [d] KOH–alumina. [e] mmol base/mmol OH^-.

intensity of the broad band at 1 110 cm^{-1}. However, the most significant change is the emergence of a strong band at 580 cm^{-1} in the main Al–O–Al stretching region. From 700 °C upwards this band begins to disappear, leaving a more regular alumina stretch at 1 000 °C.

The i.r. spectra of the 10 mmol g^{-1} KF–alumina were similarly recorded after drying at 60, 190, and 1 000 °C. The water bending region at 1 640 cm^{-1} is not so well defined and the band at 1 400 cm^{-1} is broad with two minima (1 400, 1 440 cm^{-1}), the latter of which disappears after heating above 550 °C to leave a sharp band at 1 380 cm^{-1}. The strong band at 575 cm^{-1} is very prominent in samples heated up to 750 °C. After drying at 1 000 °C the band broadens and four minima are observed (850, 760, 710, and 580 cm^{-1}). The strong band at *ca.* 580 cm^{-1} is similar to the broad Al–F stretch of hexafluoroaluminate,[12] supporting the suggestion that heating promotes fluorodehydroxylation and hexafluoroaluminate formation, especially on the higher loadings. The reduction in intensity of this band at higher temperatures suggests that the high temperature weight loss measured by thermogravimetry may correspond to loss of K_3AlF_6 as well as KF.

Surface areas of the KF- and KCl–alumina reagents were measured by a BET procedure. Figure 5 shows the loss in surface area for the reagents with increased loading and the more pronounced effect due to KF. Heating the samples up to 200 °C produced little variation in the measured surface area. However, KF–alumina samples calcined at 600 °C showed a sharp drop in surface area for both 2 and 10 mmol g^{-1} loadings. It was apparent that this loss was dependent upon the amount of water present prior to calcination as samples previously dried at 200 °C/0.1 mmHg showed a comparatively small drop in surface area upon calcination.

The impregnation of KCl onto alumina is seen to lower the surface area of alumina much less than does KF. Scanning electron microscopy of samples clearly shows KCl to be deposited upon alumina in large crystalline growths, covering the surface in a way quite different to KF deposition. The lower solubility of KCl and lack of reaction with the alumina surface presumably leads to the difference in impregnation, and the small drop in surface area due to some blockage of pores. The greater surface area loss for KF is due to the reaction of F^- with alumina and subsequent structural damage. This is most apparent for the higher loadings which contain sufficient water and KF to form an appreciable amount of K_3AlF_6 [equation (1)].

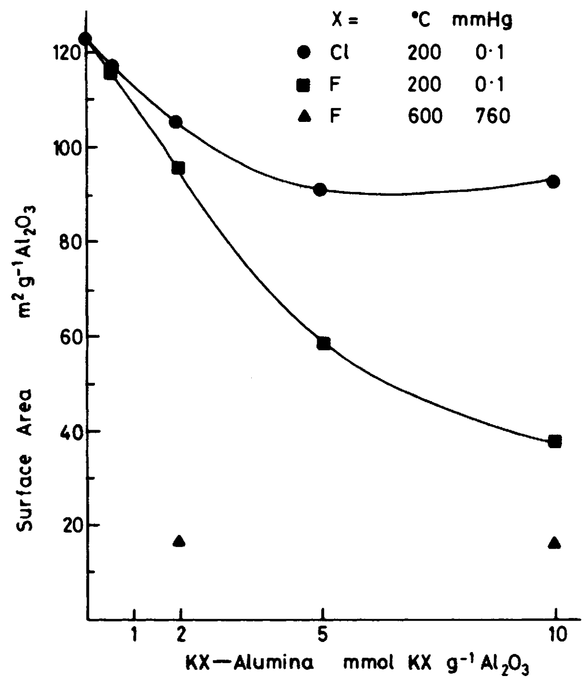

Figure 5. Experimental surface areas of KX–alumina reagents

Titrimetric analyses show that the reagents may liberate base in aqueous solution. Table 3 shows the amount of base removed from the supported reagents by an aqueous wash (column A), and this is compared with the amount of acid neutralised when the reagents are shaken with standard acid (column B). The aqueous wash basicity must be a measure of base formed by the reaction of F^- with alumina, since F^- itself it not basic in aqueous solution. If hydroxide is liberated as in equation (1), or by any other means such as the alumina-catalysed hydrolysis of KF to KOH and KHF_2, then the maximum quantity should be limited to 0.5 times the moles of KF. The consistently greater level of total basicity of the KF–aluminas, as measured by the aqueous acid neutralisation, suggests that well dispersed F^- upon Al_2O_3 behaves as a strong base without prior formation of OH^-. The fraction of the total reagent basicity which is not related to any water-soluble base (Table 3, column C) could be termed the 'fluoride basicity,' that is basicity directly arising from F^- dispersion on the alumina surface.

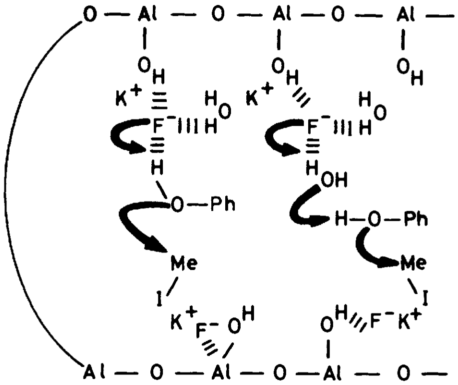

Figure 6. Possible schematic models of phenol alkylation on KF–alumina

Also shown in Table 3 is a comparison of KOH–alumina basicities for those reagents which were used in the reaction studies. The fraction of H_2O-insoluble basicity (column C), presumably due to KOH or $KAlO_2$ trapped within pores, is significantly lower than for the KF–alumina reagents, supporting the suggestion that column C mainly represents 'F^- basicity' for the latter reagents.

The amounts of base liberated from the KF–alumina reagents by aqueous washing are not sufficient to account for their high activities in base promoted alkylation. Non-aqueous titrations of MeCN washes of the reagents show that almost no basic species (F^- or OH^-) are liberated into the reaction solutions, thus the reactions must be occurring at the surface.

High-resolution solid-state n.m.r. spectroscopy has also been used for the analysis of our supported fluorides and we believe that this is the first example of the application of this technique to the study of supported reagents. Clear and unambiguous signals due to the supported F^- can be observed in the ^{19}F n.m.r. spectra of most of the materials investigated (Table 4) with the notable exception of the high-temperature-dried, low-loaded KF–alumina. In view of our interpretation of the results from the other analytical studies described here, it seems likely that this is owing to the longer relaxation time of the chemisorbed fluoride formed under these conditions. In general, the F^- signal intensity weakens with increasing drying temperature, as would be expected, although it is important to note that even after drying at 400 °C, the 2 mmol g^{-1} sample spectrum still shows the presence of F^-. It is very interesting to note that the δ_F for the KF–alumina samples is at appreciably higher field than that for the CsF–alumina samples. This is presumably due to different degrees of ion-pairing in the materials. The relatively high-field δ_F values for KF–alumina suggest that the anion is co-ordinately unsaturated since the corresponding signals for pure KF, or KF in solution, occur at significantly lower fields. We intend to exploit further this new and potentially important technique for studying these types of materials, by further and more comprehensive investigations.

Table 4. ^{19}F N.m.r. chemical shifts for KF–alumina and CsF–alumina

Reagent	Loading mmol KF g^{-1} Al_2O_2	Drying temp. (°)	δ_F (p.p.m.) (C_6F_6)
KF–alumina	0.6	110	3
KF–alumina	0.6	200	3
KF–alumina	0.6	440	
KF–alumina	2.0	120	4
KF–alumina	2.0	200	4
KF–alumina	2.0	400	4
CsF–alumina	2.0	120	47
CsF–alumina	2.0	200	46
CsF–alumina	2.0	440	
CsF–alumina	10.0	200	49
CsF–alumina	10.0	440	49

Mechanisms of MF–Alumina Reactivity and the Basic Species.—The analyses of the MF–aluminas enable some further rationalisation of the different optimum preparations found above and discussion of likely mechanisms to account for the high activities associated with the supported fluorides. We also postulate on the nature of the active basic species.

(*a*) *Catalytic reactions.* The KF–alumina reagents are extremely effective basic catalysts over a wide range of loadings and drying conditions. However, it has been noted, both here and before,[5] that very low loadings of KF and highly efficient drying produces the most active catalyst for Michael addition. The catalytic activity of the 0.6 mmol g^{-1} KF–alumina is presumably enhanced because reaction may occur within the pore structure of the alumina. The entrapment of reactants within pores may lower the entropy of activation, and unlike the case for the non-catalytic reactions, no inorganic salt by-product is deposited during reaction to cause blockage of these pores. Efficient drying may allow freer entry of the reactants into the pores. The only inactive catalytic reagents were thus the highly loaded, highly dried ones which have low surface area and/or pores blocked by KF and K_3AlF_6.

The KF–alumina catalysts were generally of similar activity to KOH–alumina reagents, containing the maximum possible amount of OH^- which could be formed by reaction of F^- with alumina [equation (1)]. Thus it was not possible to distinguish immediately whether active basic fluoride or hydroxide sites were responsible for the enhanced catalytic activity of KF–alumina. However, the titrimetric measures of the reagent basicities show them to be greater than can be explained from hydroxide formation alone. It may also be noted that the highly loaded, calcined KF–alumina reagent [which can presumably form a significant amount of OH^- by equation (1)] is very much less active than a calcined KOH–alumina one, again indicating that liberated OH^- alone does not account for the KF–alumina enhanced basicity.

Nevertheless the contribution of OH^- to the high catalytic activity of MF–alumina for the fast Michael additions cannot be ignored. The loss in effectiveness of the highly loaded, calcined KF–alumina may result from pore blockage and structural damage (giving low surface area) caused by the excessive amount of KF loaded. Any liberated OH^- may then be covered and thus inaccessible to incoming reactants. A lower loaded KF–alumina reagent did not appear to lose its catalytic reactivity after calcination, although ^{19}F MAS n.m.r. suggested that F^- was greatly reduced. Thus, an OH^--forming reaction with the alumina surface could be important for the high catalytic activity.

(*b*) *Non-catalytic reactions.* The drop in activity, and the inability of KF–alumina loadings below 5 mmol g^{-1} to assist the alkylation reaction to completion, are thought to be partly due to blockage of the active basic sites. At low loadings of KF the active basic sites are more dispersed on the alumina surface and strong adsorption of reactants may occur at unreactive surface sites. Hence addition of deactivated alumina lowered the activity of the highly loaded KF–alumina, and addition of water liberated unchanged phenol from low loaded reagents after they had apparently ceased to be effective for alkylation. The *X*-ray powder diffraction analysis showed that MI was deposited on the alumina surface during alkylation. Thus the reaction, being assisted within pores on the internal surface of the reagent, will become progressively more difficult as the metal iodide salt is deposited.

The lower reagent activities observed after loading more than 5 mmol KF g^{-1} and after continued drying may be the result of several effects. Both *X*-ray diffraction and i.r. studies of the reagents show that K_3AlF_6 is formed by the reaction of KF with alumina. Although this does not appear to cause excessive structural damage and loss in surface area upon drying to 200 °C, its formation will obviously reduce the quantity of F^- available to promote alkylation. Only the high loadings of KF furnish sufficient concentrations of F^- and water to form appreciable K_3AlF_6 [*via* equation (1)], which may be facilitated by excessive drying or by the alkylation reaction. The adsorption of reactants at inactive sites on alumina may also be enhanced by drying of the reagents. However, the reactivation of highly dried KF–alumina by the addition of water, and the fact that the 5 mmol g^{-1} optimum reagent was the highest KF loading to retain an equimolar amount of water, suggest that a partially hydrated fluoride ion species may act as a highly active basic species. The moderately dried 5 mmol g^{-1} KF–alumina has both a high surface area of well dispersed F^- and sufficient water to give the greatest coverage of these active basic sites.

Comparison of the KF- and KOH–alumina reagent activities for alkylation suggests that the high activities of the former cannot simply be owing to OH^-, formed by reaction of KF with alumina during reagent preparation. Although some activity due to this cannot be excluded, the non-catalytic activities and basicities (as measured by titrimetry) of the supported KF reagents are greater than would be expected if all the loaded KF reacted to form 0.5 mol equiv. of OH^-.

At least two types of active basic site involving F^- may be envisaged (Figure 6). For very well dried reagents, the F^- ion may be strongly H-bonded to the hydroxylated surface of alumina ($Al–[OH\cdots F]^-$). The result of this interaction will be a decrease in F^- nucleophilicity but, through good charge localisation,[13] the tightly localised centre of the negative charge may give a generally high level of basicity. Our results show that water plays an important role in determining the activity of the reagents for non-catalytic reactions. We interpret this by postulating an active basic site involving a co-ordinately unsaturated F^- ion stablised on the alumina surface which may also be H-bonded to local water molecules (Figure 6). Fluoride ion may still exert powerful basicity through a partial hydration sphere by its strong H-bonding ability. The ^{19}F n.m.r. results do not allow us to confirm the change from surface OHF^- H-bonding to partial hydration of the F^- but they do support our conclusion that the more active forms of the supported fluorides contain co-ordinately unsaturated F^- anions.

Acknowledgements

We thank BDH Chemicals Ltd. and the S.E.R.C. for their support of this work, and the Japan Society for Promotion of Science-Royal Society for a Research Fellowship (to D. G. C.). The work was also supported in part by a Grant-in-Aid from the Japanese Ministry of Education, Science and Culture. We are also indebted to the Southwestern Ontario n.m.r. facility located at the University of Guelph and to NATO for supporting the collaboration between J. H. C. and J. M. M. For powder *X*-ray analyses we are indebted to Professors M. Koizurai and S. Ueda.

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Received 13*th September* 1985; *Paper* 5/1576