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FLUORIDE-ALUMINA REAGENTS: THE ACTIVE BASIC SPECIES

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Abstract: Comparison of KF and NaF impregnated on active alumina shows that the formation of strong base by fluoride reaction with alumina cannot totally explain the extremely high reactivity of KF-alumina as a heterogeneous base for catalytic as well as non-catalytic reactions. At least three mechanisms apparently give rise to the high basicity.

While the applications and advantages of KF-Al_2O_3 reagents as heterogeneous bases for organic synthesis continue to increase[1], the reasons for the high basicity remain a point of contention. We recently showed that the nature of MF-Al_2O_3's is dependent upon the reagent preparation: mmol g^{-1} loading and drying conditions.[2,3] Powder X-ray diffraction and IR analysis clearly indicated the formation of potassium hexafluoroaluminate (K_3AlF_6), notably in samples loaded above ca. 2 mmol g^{-1}. The formation of this compound must be accompanied by formation of hydroxide and/or aluminate (Reaction 1), resulting in the contention over the nature of the actual basic species responsible for the high reactivity of KF-Al_2O_3. Weinstock etal[4] have also recently noted the presence of K_3AlF_6 in an unspecified sample of KF-Al_2O_3 and state that "fluoride ion per se has little or no direct role in the enhanced reactivity", and "potassium hydroxide and/or aluminate are the agents responsible". This prompts us to report our further studies in this field which support our previous view[2,3] that OH^- alone cannot totally explain either the high catalytic or non-catalytic activity of KF-Al_2O_3.

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

The Michael addition of nitroethane to buten-2-one has been shown to be efficiently catalysed by variously prepared KF-alumina reagents.[2,5] Only highly-loaded-highly-dried reagents gave significantly poor catalysis. In an effort to distinguish between catalysis by F^- and liberated strong base from

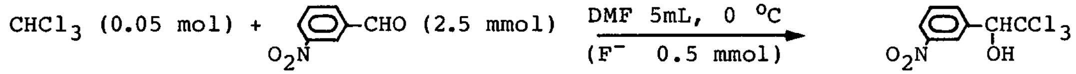
Table 1. Reactivities of similarly prepared NaF- and KF-alumina reagents

entry	reaction[a]	$MF-Al_2O_3$[b] mmol g^{-1}	time	% conversion[c] M = Na (M = K)[d]
1	A	0.6	150s; 210s; 270s	38 (40); 47 (62); 56 (69)
2		2.0		25 ; 32 (60); 39 (70)
3		5.0		9 (43); 13 (62); 15 (77)
4	B	0.6	3.0h	9[e]
5		5.0		3 (64)[e]
6	C	0.6	1.5h	1 (7)
7		5.0	1.5h; 5.0h	4 (90); 8 (100)

a) Reactions:

A = $EtNO_2$ (0.05 mol) + $MeCOCH{=}CH_2$ (2.5 mmol) $\xrightarrow[(F^- \ 0.5\ mmol)]{MeCN\ 5mL,\ rt}$ $MeCO(CH_2)_2CH(NO_2)Me$

B =



C = PhOH (0.5 mmol) + MeI (1.6 mmol) $\xrightarrow[(F^- \ 2\ mmol)]{MeCN\ 5mL,\ rt}$ PhOMe

b) Reagents dried at 90 °C/20 mmHg; Merck alumina 90, grade 1 for chromatography. c) by GLC. d) From ref. 2 for reactions A and C. e) *cf.* 98%, 1h, 0 °C with unspecified KF-alumina and reaction conditions.[4]

the F^- reaction with Al_2O_3 we have determined the activities of $NaF-Al_2O_3$'s for this reaction. Table 1 gives comparison of similarly prepared NaF- and $KF-Al_2O_3$'s as catalysts and shows that $NaF-Al_2O_3$ is only efficient at the lowest loading for reaction A. This activity was somewhat higher than expected from our previous experience with $NaF-Al_2O_3$ for non-catalytic promotion of alkylation reactions.[6] The supported alkali metal fluorides showed the same relative reactivities as the unsupported salts (Na<<K<Cs). Table 1 shows that the $NaF-Al_2O_3$ reagents are also much poorer than the similarly prepared $KF-Al_2O_3$'s for promoting phenol methylation (reaction C).[7] Weinstock *etal* used the addition of chloroform to 3-nitrobenzaldehyde to compare some $KF-Al_2O_3$ reactivities. Table 1 shows that the $NaF-Al_2O_3$'s have much lower reactivity for this addition (reaction B).

To determine the amount of liberated strong base, from F^- -- Al_2O_3 reaction, we had performed titrimetric analyses on a series of $KF-Al_2O_3$'s.[2] Aqueous washing of the reagents gives an alkaline solution, titration of which gives a guide to the amount of soluble base formed during the reagent preparation. Washing the reagents with a fixed excess of aq. HCl enables the "total basicity" of the reagents to be measured. Table 2 gives the comparison of the measured basicities for the similarly prepared NaF- and $KF-Al_2O_3$'s.

Table 2. Titrimetric analysis of NaF- and KF-alumina basicity

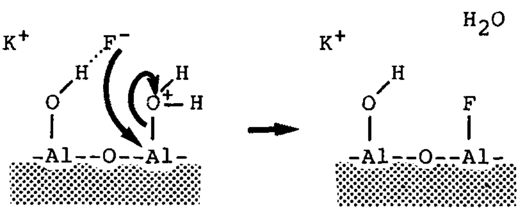
entry	reagent[a] mmol g^{-1}	aqueous wash[b] $\left[\frac{\text{mmol base}}{\text{mmol MF}}\right]$		aq. acid wash[c] $\left[\frac{\text{mmol acid neutralised}}{\text{mmol MF}}\right]$	
		M = Na;	M = K[e]	M = Na;	M = K[e]
1	0.6	0.06	0.18	0.88	0.69
2	2.0	0.13	0.21	0.86	0.81
3	5.0	0.19	0.33	0.78	0.84

a) Dried at 90 °C/20 mmHg. b) Samples (0.5 g Al_2O_3) shaken with 5 mL H_2O for 5 min. Solutions filtered and reagent rapidly washed with further H_2O before titration of combined filtrate with 0.05M aq. HCl to phenolphthalein end point. c) Samples (0.5 g Al_2O_3) shaken with 5 mL 1.0M aq. HCl for 5 min. Solutions quickly titrated with 0.2M aq. NaOH to methyl red end point. e) Ref 2.

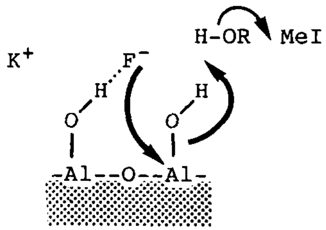
It is clear that the amount of water-soluble base on the NaF reagents does not correspond to the observed catalytic activities. Indeed the soluble base increased with increased loading whereas the activity decreased. The "total basicity" of all the reagents is extremely high, and notably higher than could be explained by simple OH^- formation (Reaction 1). Although F^- alone hardly neutralises aq. HCl at all,[2] in the presence of Al_2O_3 each F^- ion is apparently able to act as a strong base. A mechanism such as shown in Scheme 1 is consistent with this observed basicity of the reagents, and this type of co-operative basicity can also readily account for the previously observed formation of K_3AlF_6 on KF-alumina during promotion of a non-catalytic alkylation reaction,[2] Scheme 2.

Co-operative basicity of F^- and alumina

Scheme 1.



Scheme 2.



The drop in catalytic activity of the NaF-aluminas with loading may well be a result of excess salt covering active hydroxide sites, formed by the F^- -- Al_2O_3 reaction (1). However, if OH^- is the main catalytic agent the high activity of the similarly loaded KF-Al_2O_3's is somewhat inexplicable. Although these reagents contain a little more OH^- (Table 2) they should experience a similar MF salt coverage effect.[3] We envisage that F^- itself may become a strongly basic catalytic species if it is co-ordinately unsaturated. Evidence to suggest the presence of such ions has been obtained by ^{19}F MAS NMR of these reagents.[2,8] Strong ion pairing of NaF appears to inhibit catalysis by the NaF salt coverage, but the weaker ion pairing of KF and CsF allows F^- to become active for promoting both catalytic and non-catalytic reactions. The extremely small amount of base washed from the active NaF-Al_2O_3 loaded at 0.6 mmol g^{-1}, but the high "total basicity" of the reagent as measured by its ability to neutralise aqueous acid, may mean that even NaF can be activated if the salt is sufficiently well dispersed over the alumina surface to reduce ion pairing and leave some F^- sites co-ordinately unsaturated. Certainly dispersing the salt over more alumina surface will increase the number of sites where F^- is able to act as a base through interaction with the surface, as in scheme 2.

In summary we should like to stress that KF-alumina does not owe its basic activity solely to the formation of potassium hydroxide and/or aluminate during preparation. Not only does this reaction give insufficient base to promote the non-catalytic reactions, it appears that the strong base is mostly covered by a further layer of KF when loading is above *ca.* 0.6 mmol g^{-1} (theoretical "monolayer" coverage of salt over the hydroxylated Al_2O_3 surface[2]), and this prevents OH^- acting as a catalyst on the higher loaded reagents. KF-Al_2O_3 thus owes its efficient and versatile reactivity as a heterogeneous base for organic synthesis to at least three possibly mechanisms: dispersion and increased surface area of KF giving co-ordinately unsaturated F^-; liberation of strong base during preparation; and the co-operative action of F^- and the hydrated alumina surface.

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