Surface Analysis of MF-Aluminas and Related Supported Reagents by Scanning Electron Microscopy

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Synopsis. SEM of MF-aluminas (M=Na, K, and Cs, loaded at 2 mmol g^{-1} and dried at 90 °C/2.7 kPa), showed similar salt dispersions and surface morphologies, with salt clusters of ca. 1 μm diameter evident on the external surfaces. Less reactive, highly dried or highly loaded, reagents showed extensive surface crystallization. KCl- and KOH-aluminas showed the effect of anion basicity, giving greater clustering and surface destruction respectively.

Although supported inorganic salts have been employed in a wide variety of organic reaction types, [1,2] only in a few recent cases has the full potential of improved reagent selectivity, reactivity and stereospecificity begun to be realized, by careful study and optimization of predispersed reagent preparations.[3,4]

KF-Alumina is a most noteworthy supported reagent which acts as an efficient and convenient heterogeneous base.[5–7] We have previously shown that different loading and drying conditions can produce quite large changes in chemical reactivity, notably for noncatalytic base promoted reactions,[7] and that supported alkali metal fluoride reagents show the same cation effect on activity as do the unsupported salts (NaF≪KF<CsF).[5] The reasons for the dramatic increase in MF basicity, when impregnated on Al_2O_3, and the subsequent reactivity variations have remained somewhat obscure despite IR, solids NMR, thermal, titrimetric and surface area analyses being performed.[7] The active basic species may involve a coordinatively unsaturated fluoride ion center, exhibiting basicity through its strong H-bonding capacity, but the basicity of species formed by reaction of F^- with Al_2O_3 cannot be discounted. In order to directly observe the effects of MF salt impregnation on the Al_2O_3 surface morphology and allow comparison with some related salts, we have now used scanning electron microscopy (SEM).

For the neutral chromatographic grade γ-alumina used, a 2 mmol g^{-1} loading of salt is calculated to give an approximate theoretical "monolayer" of ion pairs over the hydroxylated surface.[8] Although KF-alumina "monolayer" loadings and lower gave highly efficient basic catalysis, the optimum reagent preparation for a noncatalytic *O*-methylation of phenol involved a significantly higher loading (5 mmol g^{-1}, dried at 90 °C/2.7 kPa),[7] suggesting that surface coverage of salt, and active basic sites, are not maximized at the 2 mmol g^{-1} loading. Whereas X-ray powder diffraction of the reagents reveals little at these loadings (only at ca. 10 mmol g^{-1} does it give clear evidence for KF clustering and fluoroaluminate formation by chemisorption[7]), SEM directly shows the extent of salt clustering and surface deterioration.

A sample of deactivated alumina (aqueous washed, dried at 90 °C/2.7 kPa) shows that most of the particles have generally smooth surfaces (Fig. 1a) at magnification which cannot reveal their porous structure. Comparison with KF-alumina (Fig. 1b) at the 2 mmol g^{-1} loading, clearly shows the salt, in microcrystalline clusters of 0.5—1 μm diameter, well dispersed over the external surface. Microclusters of this size must contain in the order of 10^{10} KF ion pairs suggesting that a large amount of the 2 mmol of KF loaded is accommodated on the external surface in such clusters. It thus seems evident that "monolayer coverage" is not being obtained at this level of loading, and the 5 mmol g^{-1} KF-alumina may owe its optimum activity to the greater amount of KF available; a) to achieve greater coverage of the internal surface and b) to further cover the external alumina surface with salt microclusters. For reactions such as phenol alkylation, strong surface adsorption of reactants may well

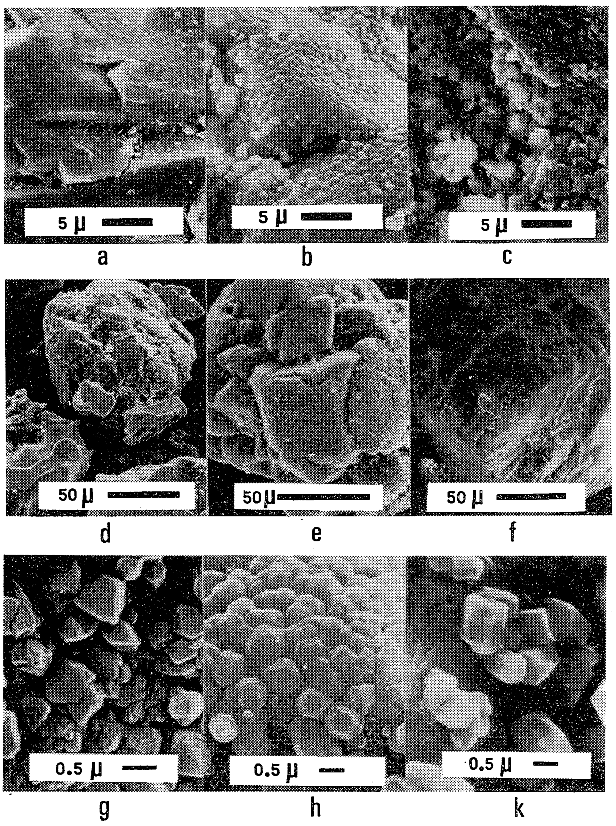

Fig. 1. Scanning electron microscopy of: (a) alumina, water washed and dried at 90 °C/2.7 kPa; (b), (e), and (h) KF-alumina 2 mmol g^{-1}, dried at 90 °C/2.7 kPa; (c) KF-alumina 2 mmol g^{-1}, dried at 600 °C; (d) KCl-alumina 2 mmol g^{-1}, dried at 90 °C/2.7 kPa; (f) KOH-alumina 2 mmol g^{-1}, dried at 90 °C/2.7 kPa; (g) NaF-alumina 2 mmol g^{-1}, dried at 90 °C/2.7 kPa; (k) CsF-alumina 2 mmol g^{-1}, dried at 90 °C/2.7 kPa.

hinder reaction if it takes place at unactive sites. Thus elimination of these sites, by more complete KF coverage, will be important for obtaining optimum reagent reactivity.[7]

Drying KF–alumina at up to 200 °C/13 Pa produced only limited local crystallization of the salt clusters, however 600 °C calcination produced a drastic change in the surface morphology (Fig. 1c) as chemisorption of KF is promoted. The surface crystallization is accompanied by a large drop in surface area (from 96 to 18 $m^2 g^{-1}$ Al_2O_3), a loss of noncatalytic activity, and also is associated with the detection of K_3AlF_6 by X-ray powder diffraction.[7]

Comparison of the alumina-supported potassium salts, KCl, KF, and KOH at 2 mmol g^{-1} loading (Fig. 1d, e, and f) shows the effect of salt basicity and surface affinity on the salt loading. The weakly basic chloride has little affinity for the alumina surface and the majority of the salt is deposited in large crystalline clusters of irregular size and shape, up to ca. 10—50 μm dimension. In contrast the highly basic hydroxide is deposited on the alumina surface in a fairly regular manner which produces some severe erosion of the surface, presumably by aluminate formation. The KF–alumina appears intermediate in terms of both the clustering of external salt, and the degree of surface damage caused by chemisorption reaction. Adsorption of KF causes little apparent surface erosion for the reagents dried at 90 °C.

The sequence of alumina-supported alkali metal fluorides, NaF, KF, and CsF at 2 mmol g^{-1} loading (Fig. 1g, h, and k) show that in all cases the external surface is covered with well dispersed microcrystalline clusters, of approximately 1 μm dimension. Although there is a large variation in the aqueous solubilities of these fluorides, increasing ca. 100 times in the above order, the similar appearance of the reagents suggests that the rate of salt precipitation onto the surface, during preparation by aqueous evaporation, does not greatly influence the cluster size and distribution. Rather, the high surface affinity of fluoride seems determinant. The clusters on all of these reagents must contain much of the salt loaded, but they do represent much smaller particles than could be obtained by conventional grinding procedures, consequently the reagents have a high salt surface area. The cation effect on the reactivity of the reagents is also in agreement with small salt clusters, rather than highly dispersed ion pairs, being responsible for the basicity.

Samples of KF- and KCl-alumina loaded at 10 mmol g^{-1} showed distinctly different external surface morphology, the fluoride having multilayers of clustered salt particles (2—3 μm size), whilst the chloride had relatively few crystal growths, covering large areas (typically 100—1000 μm^2). The greater interaction of KF, than KCl, with the alumina is also apparent in the measured BET surface areas of the two reagents.[7] KF–Aluminas continue to lose surface area with loading (38 $m^2 g^{-1}$ Al_2O_3 at 10 mmol g^{-1}) whereas the KCl–aluminas only lose surface area due to blockage of small pores, thus loadings at 2 and 10 mmol g^{-1} have quite similar surface areas, 104 and 93 $m^2 g^{-1}$ Al_2O_3 respectively.

In summary, SEM analysis has directly shown that $MF–Al_2O_3$ reagents possess most of their salt in microcrystalline clusters, which nevertheless are far smaller particles than would otherwise be obtainable. The KF salt dispersion and the $KF–Al_2O_3$ surface deterioration are intermediate between those of KCl- and $KOH–Al_2O_3$'s further supporting the idea, from the reactivity order dependence on the MF cation ($Na \ll K < Cs$), that the supported reagent basicity largely originates from a great increase in salt surface area. Thus the enhanced basicity of $MF–Al_2O_3$ reagents would seem to be more a result of improved fluoride ion strong H-bonding ability than of $F^-–Al_2O_3$ reaction generating an alternative strong base.

Experimental

Preparation of Samples. The supported reagents were prepared by adding 5 g of alumina (Merck 90, neutral for chromatography) to the calculated weight of salt dissolved in ca. 30 ml of water, followed by rotary evaporation at ca. 50 °C and subsequent drying under the stated conditions (Fig. 1). Samples were mounted with double-sided sticky tape and coated with 10—15 nm of gold[9] in an evaporative ion coater. Observation by SEM was accomplished with a Hitachi S-500AS microscope operating at 15—25 kV accelerating voltage.

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References

1) A. McKillop and D. W. Young, *Synthesis*, **1979**, 401, 481.

2) G. H. Posner, *Angew. Chem. Int. Ed. Engl.*, **17**, 487 (1978).

3) A. AlJazzaa, J. H. Clark, and M. Robertson, *Chem. Lett.*, **1982**, 405.

4) J. H. Clark and C. V. A. Duke, *J. Org. Chem.*, **50**, 1330 (1985); and unpublished results.

5) T. Ando, J. Yamawaki, T. Kawate, S. Sumi, and T. Hanafusa, *Bull. Chem. Soc. Jpn.*, **55**, 2504 (1982); J. Yamawaki, T. Kawate, T. Ando, and T. Hanafusa, *Bull. Chem. Soc. Jpn.*, **56**, 1885 (1983).

6) J. H. Clark, D. G. Cork, and M. S. Robertson, *Chem. Lett.*, **1983**, 1145.

7) 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. 2*, **1986**, 1133.

8) Alumina BET surface area is 125 $m^2 g^{-1}$ Al_2O_3 and the estimated density of surface hydroxyl groups is 8—10 nm^{-2}.

9) Samples prepared for observation in "aquadag" carbon paste, without gold coverage, showed similar results but images generally suffered from charging effects.