Tetrahedron Letters,Vol.27,No.33,pp 3845-3848,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

CHARACTERIZATION OF THE ACTUAL CATALYTIC AGENT IN POTASSIUM FLUORIDE ON ACTIVATED ALUMINA SYSTEMS

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Abstract: The spectral and chemical properties of potassium fluoride on activated alumina, an extensively used basic catalyst in organic synthesis, show that its unusually high reactivity relative to other fluoride-containing basic systems is due to the reaction of the fluoride ion with alumina to produce potassium hexafluoroaluminiate, potassium hydroxide and potassium aluminate. The reagent, more simply prepared from alumina and KOH, catalyzes the high-yielding addition of chloroform to m-nitrobenzaldehyde without producing Cannizzaro side-products.

Fluoride ion is useful as a weakly basic, non-nucleophilic catalyst in many organic chemical processes involving hydrogen abstraction or hydrogen bond formation[1]. We judged that fluorides could be potentially useful as a basic catalyst in the addition of chloroform to m-nitrobenzaldehyde to replace classical methods employing hydroxide base which give large amounts of Cannizzaro side-reaction[2]. Sources of fluoride that have been previously used include alkali metal fluorides, tetra-alkylammonium fluoride salts and various solid supported systems[1]. Among the supported fluoride systems, potassium fluoride (KF) on activated alumina[3-7] has been found to be considerably and surprisingly more reactive than non-supported KF, KF-silica gel, KF-celite or KF-molecular sieves. The versatility of KF-alumina has been demonstrated

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in the recent literature which includes accounts of its use in the Michael addition[10,14-16], Knoevenuagel condensation[11-14,16], C-,N-,O- and S- alkylation reactions[3-9], aldol condensation[13,16], Wittig reaction[11,12], Wittig-Horner reaction[11,12], Darzens condensation[12], nitrile hydration[17], Henry reaction[19] and elimination reactions[16]. KF on alumina has also recently become commercially available.[20]

The catalyst was very effective in our intended application, the addition of chloroform to m-nitrobenzaldehyde to produce α-trichloromethyl-(3-nitrophenyl) carbinol, giving a 98% conversion and 82% isolated yield with no Cannizzaro products after one hour at 0° in DMF. Continued use and scale-up of this catalyst system, however, revealed large batch-to-batch variations in activity. Upon investigating the nature of this problem via Raman and infrared spectroscopic studies of the catalyst surface it became apparent that fluoride ion per se has little or no direct role in the enhanced reactivity of KF-alumina. A reaction of aqueous KF and alumina occurs, resulting in the formation of potassium hexafluoroaluminate and a strongly basic surface consisting of potassium hydroxide and potassium aluminate. The latter agents are responsible for both the increased base activity and the variable activity, a consequence of carbonate formation.

The infrared spectrum (KBr pellet; Nicolet 7199 FTIR) of a typical KF-alumina catalyst shows, in addition to features due to alumina and water, bands readily assigned to potassium carbonate (bands at 706, 883, 1060, 1365, 1450 and 1470 cm^{-1}). We were of course initially puzzled by the presence of carbonate. An intense band at 570 cm^{-1} was also observed. To establish the identity of the species with the infrared band at 570 cm^{-1}, additional vibrational information was obtained using Raman spectroscopy. Besides an intense feature at 1063 cm^{-1} which is due to the carbonate ion symmetric stretch, the Raman specturm of a typcial KF on activated alumina sample contains weaker low frequency bands at 546 cm^{-1} and 325 cm^{-1} which, together with the infrared band at 570 cm^{-1}, were enough to establish the presence of substantial amounts of hexafluoroaluminate ion. The hexafluoroaluminate identification was made on the basis of spectral data and assignments made by Reisfeld[18].

The reaction leading to hexafluoroaluminate upon addition of aqueous KF to alumina also produces large amounts of hydroxide and therefore a much more basic system:

$$12\ KF + Al_2O_3 + 3\ H_2O \longrightarrow 2\ K_3AlF_6 + 6\ KOH$$

The increased basicity explains the formation of large amounts of carbonate upon drying and handling in air. The amount of carbonate on the catalyst was greatly reduced when the catalyst was dried in a nitrogen atmosphere. Alternatively, samples dried in a CO_2 atmosphere showed complete bicarbonate formation. The fact that KF on activated alumina systems are highly basic is confirmed by Hammett indicator measurements which indicate that the surface pKa is between 12 and 15. Potassium hydroxide and/or aluminate are the agents responsible for the unusually high catalytic activity of KF-alumina[21]. The other possibilities, potassium carbonate and potassium hexafluoroaluminate were shown to have only very weak activity in the reaction of chloroform with m-nitrobenzaldehyde. On the other hand, when aqueous KOH is added to alumina[22] to give a surface basicity similar to that observed with KF-alumina systems (total base content _ca_. 2.8 meg/g by titration) the catalytic activity in terms of conversion and rate are comparable (99% conversion, 81% isolated yield, 1 hour 0° in DMF).

Potassium fluoride on _non_-activated alumina fails to form potassium hexafluoroaluminate and a strongly basic surface; it exhibits only weak activity in the chloroform addition reaction (18% conversion after 3 hours at 0°). We also examined KF on Celite and found no unusual catalytic activity or chemical reaction analogous to KF on activated alumina.

In conclusion, it has been shown that the enhancement of reactivity of fluoride when supported on activated alumina is a consequence of hydroxide and/or aluminate formation. The reagent can be prepared directly by adding KOH to alumina. It is noteworthy that little or no Cannizzaro products are detected when KOH-alumina catalyzes the addition of chloroform to m-nitrobenzaldehyde in contrast to solid KOH or phase transfer conditions[2].

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21) Extraction of KF on activated alumina with water under an inert atmosphere produced a strongly alkaline filtrate which deposited a gelatinous precipitate of $Al(OH)_3$ upon neutralization. Titration with HCl showed the presence of hydroxide (ca. 1.8 meq/g) in addition to a second strong base (ca. 2.7 meq/g) about two log units lower than hydroxide and small amounts of carbonate (ca. 0.01 meq/g).
22) A mixture of 30 g of activated alumina, 50 ml of water and 28 g of KOH is stirred 1 hr at 70°, filtered at 40° and sucked to a free-flowing powder under nitrogen.

(Received in USA 25 April 1986)