

Reactions on fluorinated surfaces

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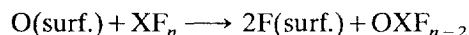
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The use of metal fluorides as heterogeneous catalysts in fluorine chemistry is well established, partly due to the pioneering work of G.H. Cady and his coworkers [1]. Fluorinated oxide surfaces are also important; the reactions which describe the fluorination of a hydroxylated oxide surface, for example



and



are very simple but the effects produced can be subtle. Impregnation of γ -alumina with KF results in a strongly basic material. Fluorination to give K_3AlF_6 also occurs; possible candidates for the other product are either KOH [2] or deprotonated $\text{Al}-\text{O}^-$ (surf.) sites [3]. The latter explanation appears to be more consistent with the observations made when KF or CsF supported on γ -alumina are subjected to surface fluorination using reagents such as SF_4 , OSF_2 or HF, in the latter case after SO_2 pretreatment. The Group I fluorides supported on fluorinated γ -alumina are good catalysts for the room-temperature chlorofluorination of SF_4 , an excellent model reaction for the study of F^- catalysts [4]. The adsorption behaviour of $^{35}\text{SF}_4$ and ^{36}ClF [5], yields of SF_5Cl and kinetic studies in which the disappearance of ^{36}Cl or ^{35}S surface radioactivities are monitored [6] are all consistent with maximum catalytic activity at MF loadings of 5.5 mmol g^{-1} . The activity of supported CsF is comparable with that of unsupported material and reaction mechanisms appear to be identical (cf. Ref. [7]).

The role of surface fluorination in a non-catalytic situation is illustrated by the chemomechanical polishing of a silica glass surface. Addition of $[\text{HF}_2]^-$ to a polishing reagent, based on a CeO_2 suspension in water at low pH, accelerates the polishing reaction without detriment

to the quality of the surface finish. In contrast, addition of $[\text{HF}_2]^-$ to an alkaline silica sol reagent has no effect. The difference reflects the change in properties of the SiO_2 surface with pH change. Polishing or etching under acidic conditions with $\text{CeO}_2/\text{K}[\text{HF}_2]$ leads to the formation of a surface layer, readily visible by optical microscopy or SEM, which has been identified from a detailed spectroscopic and radiotracer study as K_2SiF_6 coated with hydrated silica [8]. The reaction sequence proposed is surface fluorination, followed by hydrolysis, followed by mechanical wiping of the surface to remove the layer.

The high-quality surfaces so produced are excellent substrates for the vacuum deposition of thin organic films. This is illustrated by the electronic spectra of films derived from polycyclic aromatic hydrocarbons, chemically modified by treatment with AsF_5 or MoF_6 .

Acknowledgements

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