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Letter to the Editor

Silanol groups on silica gel

The ideas concerning multilayer adsorption of water on the surface of silica gel by Scott and Traiman[1] and in a very similar article by Scott[2] seriously differ from the ideas of most other workers in this field. In this letter I am pointing out these differences but will make no further reply or rebuttal.

The ideas of the above authors are based on the false assumption that the total number of silanol (SiOH) groups on the surface of silica gel corresponds to the number of trialkylchlorosilane molecules that can react with the surface and that any further water that is evolved by subsequent heating must therefore be present as "adsorbed" water.

It has been generally concluded by other workers that the hydrated surface of amorphous silica dried at 150°C in air has from 4.5 to 8.0 SiOH groups/nm^2. This corresponds to about 8 to 13 μmoles/m^2. I have summarized past studies in ref. 3.

Only a fraction of the silanol groups can react with trialkyl chlorosilane because the size of the trialkylsilyl group is so large that only 1.8 to 2.4 are required to cover 1 nm^2. The remaining silanol groups remain unreacted under the umbrella-like groups. Thus if 1 nm^2 (= 100 A^2) of surface bears 8 SiOH groups and only 2 trialkylsilyl groups can react with 2 SiOH groups, there will remain 6 SiOH groups under the outer layer of hydrocarbon groups.

Apparently Scott believes that there are no more silanol groups left and that the water that is evolved when the silica is heated to higher temperature must have been present as "adsorbed" water.

When the surface of silica is esterified by reaction with an alcohol to give a hydrophobic surface, only part of the silanol groups can react, just as in the case of reaction with trialkyl chlorosilane. This has been shown by analyses of the silica for total hydrogen and carbon before and after esterification[4].

Scott refers to the unreacted silanol groups as the "first layer of strongly hydrogen bonded water" that is held on the original surface up to 200°C and is not removed by hydrogen bonding solvents.

The problem may be one of terminology, but if so, this can lead to serious misconceptions. There is a real and important difference between "water molecules adsorbed by hydrogen bonds" and "silanol groups on the surface that can interact and form water at temperatures above 200°C". The statements within quotation marks express the two differing point of view.

I fully support the views of Snyder and Poppe[5] who discussed this matter more fully now.

As to the true multilayer adsorption of water, see Pashley[6].

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