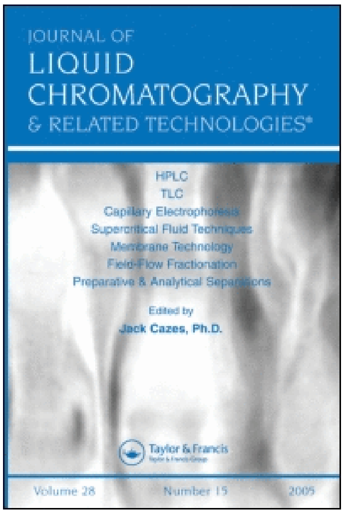

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ANALYSIS OF CHEMICALLY BONDED SILICA GEL BY COMPUTATIONAL CHEMISTRY

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ABSTRACT

Several forms of silica gels were constructed by Molecular Mechanics calculation. The structure of a designed silica gel is limited because of the requirement of physical strength and the maximum bonding. The number of silanol groups was a half that of the silicon atoms on the surface of the silica gels. All the silanol groups can be completely silanized with chloro- silane reagent to make a chemically stable bonded phase from the theory.

INTRODUCTION

Octadecyl bonded silica gel (ODS or C18) is the most popular packing material in liquid chromatography like methylsilicone phase capillary column in gas chromatography. Much effort has been invested in synthesizing an ideal ODS packing. The basic requirements are stability and reproducibility. Improving the purity of silica gel enhanced physical strength due to the homogeneous structure and the reactivity of silyl reagents due to lack of interruption by metal ions.

A porous silica gel of purity greater than 99.99% was silanized with octadecyl chlorosilane and trimethylsilylated. Inertness and stability tests were proposed [1,2]:

1. The peak for pyridine which is an indicator of reactivity with silanol groups, and whose reactivity is stronger than that of aniline, had to be eluted before the peak of phenol.
2. Benzoic acid, which is an indicator of the existence of nitrogen compounds on the surface of chemically bonded silica gel, had to be eluted with a good peak shape.
3. 8-Hydroxyquinoline which is a very active chelate reagent, had to be eluted as a sharp peak.
4. The ODS packing had to be stable for over 500 hours immersion in both 0.1% trifluoroacetic acid solution and 0.01M disodiumphosphate in 40% aqueous methanol solution.

Further studies have been performed to synthesize packings which are more stable and easier to handle. The stability was improved by more than 5,000 hours immersion in 0.1% trifluoroacetic acid solution. Batch to batch distribution of carbon content is less than 5% and the deviation of capacity ratio of standard compounds is also less than 5%. The surface of the bare silica gel was very smooth as seen under by the analysis of an electron micro scope, and the possible structure of the silica gels and the reactivity of silanol groups were analyzed with the aid of computational chemistry to improve the performance of newly bonded packings.

EXPERIMENTAL

The Molecular Mechanics calculation was done by CAChe from Sony-Tektronix (Tokyo, Japan), and the computer was a Macintosh IIfx.

RESULTS AND DISCUSSION

Silica gel is a polymer of SiO2, and SiO2 can form different polymer shapes such as in fiber, sheet, column, non-porous and porous materials [3]. When the -Si(H2)O- unit was polymerized, it formed a spiral fiber as seen in Fig. 1, and when the -SiH(OH)O- unit was polymerized, it also formed a spiral fiber as seen in Fig. 2. These polymers may not form a physically strong porous packing.

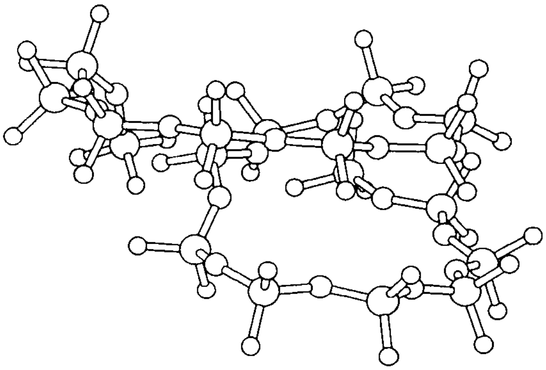

Fig. 1 Polymerized -Si(H2)O- groups optimized by Molecular Mechanics calculation. The largest circles are silicon atoms, middle size circles are oxygen atoms, and the smallest circles are hydrogen atoms.

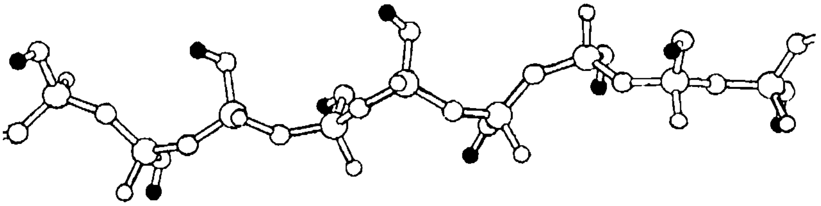

Fig.2 Polymerized -SiH(OH)O- groups optimized by Molecular Mechanics calculation. Closed circles are hydrogen atoms of silanol groups, others are the same as those in Fig. 1.

Three SiO2s can form a ring. This ring can be considered a basic unit for making a porous silica gel. When these rings were polymerized in the horizontal direction, a silica gel column could be synthesized as shown in Fig. 3, however this column may have only a few silanol groups at the ends. If the siloxane structure is broken to make silanol groups, it makes the physical strength weaker, and this means it is not an ideal structure as a porous silica gel packing.

When the rings were polymerized in the vertical direction, polymerized sheet or pillar could be synthesized from four rings as one unit as shown in

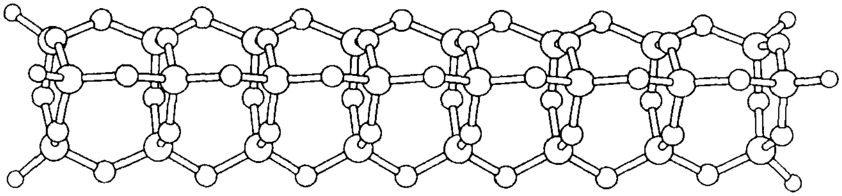

Fig. 3 Polymerized [(SiO2)3]n, n=8. Circles: see Fig. 1.

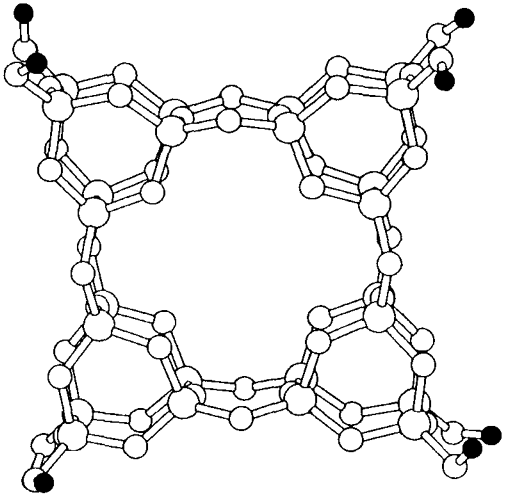

Fig. 4 Tree dimensionally fused rings. Circles: see Fig. 2.

Fig. 4. However the large unit has a few silanol groups which form physically strong polymers.

Six SiO2s can also form a ring which can grow into a three dimensional polymer. In this large unit, all silicon atoms have two free valences to join together. 50% of the silicone atoms have free silanol groups which can be silanized on the surface of the polymerized structure. The distance between the oxygens of two silanol groups is 3.78 - 5.47 Å as shown in Fig. 5. The shortest distance between the two chlorines of a silylating reagent is 3.43 Å, similar to this distance. The number of silanol groups can be increased by splitting siloxane on the surface, however the atomic distance of silanol

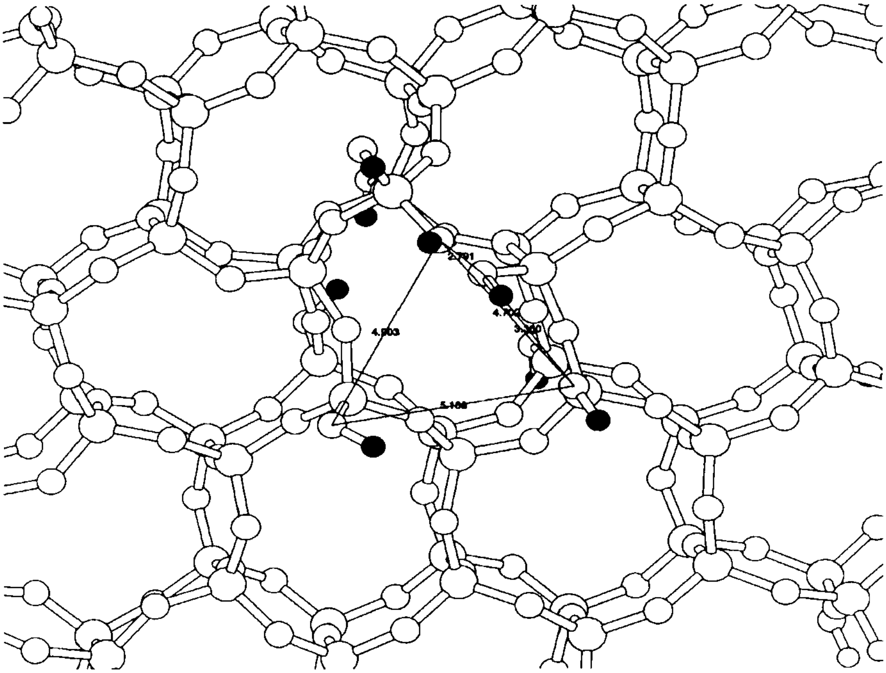

Fig.5 Atomic distance between the oxygens of two silanol groups of six SiO2s. Circles: see Fig. 2.

groups is not ideal for trichlorosilane. This means that three functional bonding can not be formed smoothly , and the splitting of too many siloxane will make the porous structure weaker.

As the ideal surface structure, one of two silicon atoms has one silanol group which can be silanized by either mono- or di- or trichlorosilane. No free silanol group is on the bonded surface after the silanization, and the bonded surface does not require further silanization. The surface of the silica matrix is completely covered by the bonded organic phase which can protect the corrosion of silica gel itself by acid or basic solutions. If the silanol groups are not completely silanized by the first reaction, a second silanization process, end-capping, is required. The carbon content did not significantly increase in this end-capping process.

When more than seven SiO2 form a large unit ring, the center hole is large enough to collect and keep a metal ion in it, but not large enough for total silanization, and the structure of the polymer may not be homogeneous. This means that the porous silica gel will be physically weak, and does not have an ideal surface for total silanization.

The real structure of porous silica gel is unknown, however electron microscopic analysis indicates a smooth surface. The bonded silica gel made form pure silica gels was very chemically stable compared to that by ordinary silica gels. This means that the purer the silica the more homogeneous is the structure improves the physical strength and the reactivity of silanization. The basic structure may be based on rings of six SiO2s.

According to the literature, all silicon atoms on the surface can be converted to silanols, and 50% of the silanols can be silanized. The steric effect of silylating reagent was analyzed by X-ray crystallography. However, in the above newly designed silica gel, it appears that only 50% of silicon atoms on the surface are silanols, and that all the silanols can be silanized. Although the surface coverage can be estimated from the carbon content, the surface area and the pore size, the proposed inertness test is more practical for measuring the surface coverage than calculation from physical properties.

When stable bonded phases become popular packings, the specification of the packings will be useful like the McRaynolds constant for the liquid phase of gas chromatography. The octadecyl or octyl bonded phase will be related to the methylsilicone phase, the phenyl bonded phase may be 5% phenylmethylsilicone phase, the polystyrene gel may be a 100% phenyl silicone phase and cellulose may be a Carbowax phase. In future, precision of selectivity of bonded phases will be obtained by the aid of computational chemistry [4]. Further development of stable packings and increased selectivity of measurement methods are required.

REFERENCES

1. T. Hanai, M. Ohhira and T. Tamura, LC-GC, 6, 922 (1988).
2. M. Ohhira, F. Ohmura and T. Hanai, J. Liq. Chromatogr., 12, 1065 (1989).
3. G. Alexander, Silica and I, translated by K. Inoue, Tokyo Kagaku Dojin, Tokyo 1971.
4. T. Hanai, J. Chromatogr., 550, 313 (1991).

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