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CHEMICAL MODIFICATIONS OF SILICA SURFACES

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13. ABSTRACT

The purpose of the work was to modify the surfaces of silicas by chemical means, i.e. by causing them to react with gaseous or liquid materials under controlled conditions, in order to alter the nature and reactivity of the surfaces. The reactions and the molecular species occurring on the surfaces were to be monitored by means of infrared spectroscopic techniques.

An entirely new type of surface defect has been discovered. The defect has the properties expected for a center consisting of two closely-spaced silicon radicals associated with two anomalously reactive oxygen atoms.

The defect responsible for the activity of reactive silica (RS) is best produced by a methoxylation, pyrolysis, degassing procedure. Materials having some of the properties of RS can be produced by treating silicas with certain silanes.
RS and its reactions provide an extremely interesting and entirely novel aspect of the chemistry of siliceous surfaces.

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Surface properties
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CHEMICAL MODIFICATIONS OF SILICA SURFACES

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PURPOSE

The purpose of the work was to modify the surfaces of silicas by chemical means, i.e. by causing them to react with gaseous or liquid materials under controlled conditions, in order to alter the nature and reactivity of the surfaces. The reactions and the molecular species occurring on the surfaces were to be monitored by means of infrared spectroscopic techniques.

RESULTS

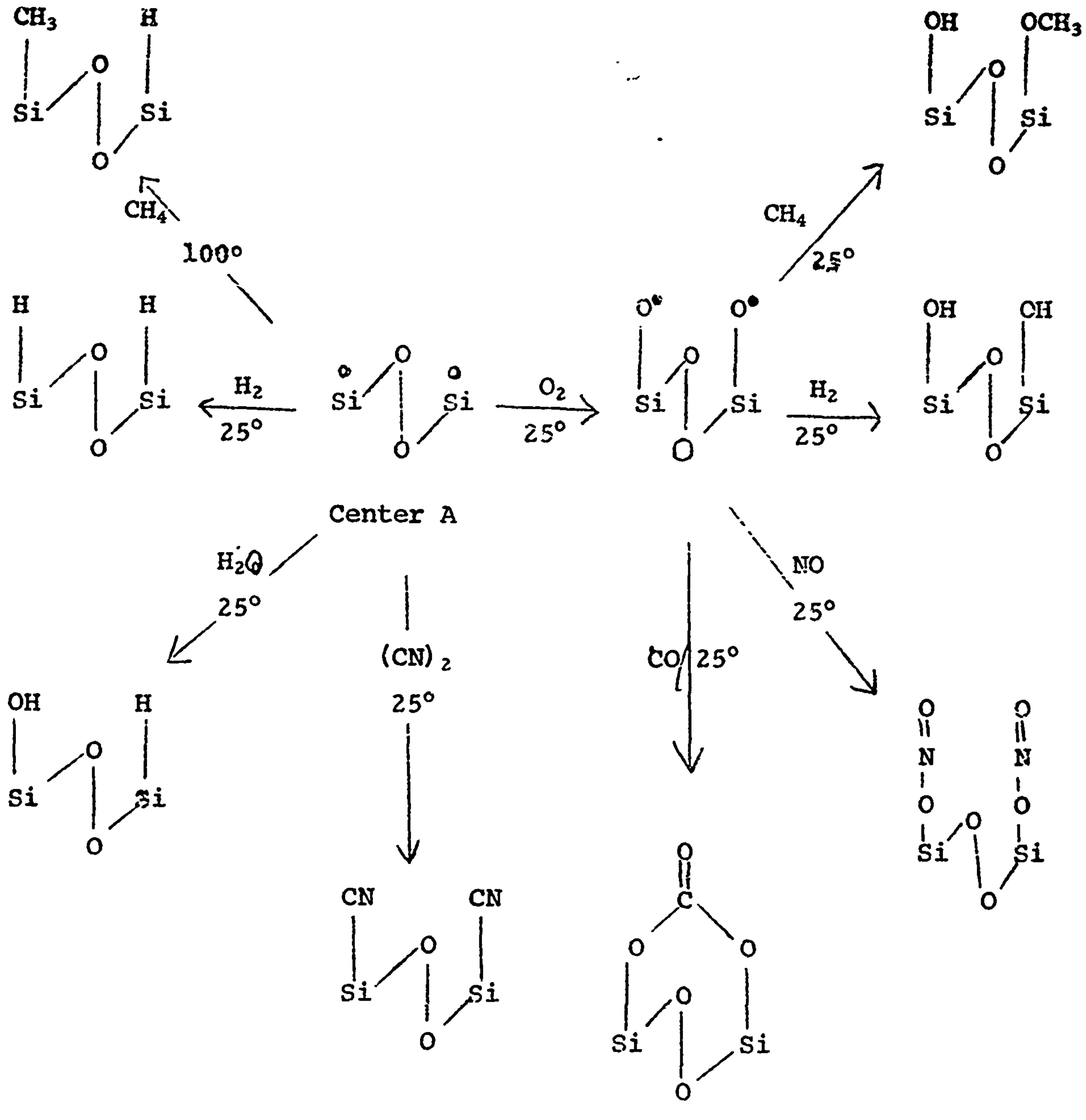
It had been found that when high surface area silica was subjected to a three-step treatment consisting of methoxylation, pyrolysis of the surface methoxy layer, and degassing at high temperature, a totally new and remarkable adsorbent was formed (C. Morterra and M.J.D. Low, J. Phys. Chem. 73, 321, 327 (1969). The new new material was termed Reactive Silica (RS) for brevity. Unlike ordinary silica, RS would chemisorb hydrogen dissociatively at room temperature; ≡Si-H groups were formed in addition to the $=SiH_2$ groups already existing on the RS surface. As RS seemed to be a promising material (e.g., the surface $=SiH_2$ groups were stable in air to 350^{0}C), work was carried out to (a) find out what was responsible for the unusual behavior of RS, and (b) search for alternative methods of preparing RS.

The Nature of RS

In order to find out what made RS reactive, experiments were carried out in which RS samples were caused to react with NH_3 and with CH_4. Also, other research programs in the Principal Investigator's laboratory supplied information about the interaction of RS with H_2, O_2, CO, H_2O, NO, C_2H_2, and $(CN)_2$. The various results have included quantitative gas adsorption measurements, electron spin resonance and infrared spectroscopic data and have permitted an almost complete formulation of the mechanism. The salient features are as follows:

The unusual and remarkable reactivity of the material we term RS is due to a small number of reaction centers. These are geminal in nature and consist of pairs of silicon radicals less than 4 Å apart. Each center is associated with two oxygen atoms which show anamalous behavior, i.e. the two oxygen atoms are not those of "normal" siloxane bridges on the silica surface, but behave as if a peroxo bridge linked the two sites. The number of the geminal centers is small, about $10^{13}/cm^2$ of surface. The geometry and reactivity suggest that the reaction centers are formed at a step on the silica surface.

The various chemical properties of the center are schematically represented by a grouping A. Some of the reactions of A are outlined by the mechanism summary below.



It will be recognized that the reactions are highly unusual and that the active center A is unusual, also. Such centers have not previously been postulated or found.

Preparation of RS

A series of tests have been carried out to see if RS could be prepared by methods other than the methylation/pyrolysis procedure. Some of the tests were as follows.

Method 1. Degassed silica is exposed to tetramethoxysilane (TMS). The TMS in part reacts with residual hydroxy groups present on the silica surface and becomes dissociatively chemisorbed. High temperature pyrolysis and degassing then leads to a collapse of the surface methoxy group and to the formation of RS.

Method 2. Degassed silica is exposed to trimethylchlorosilane (TMCS). At temperatures above 200°C there is a dissociative chemisorption. High temperature degassing then produced RS.

Method 3. This is similar to Methods 1 and 2, but involves the reaction of Trimethylsilane.

Method 4. Trivinylchlorosilane is reacted with silica at temperatures above 300°C, when a dissociative chemisorption occurred. Pyrolysis then disrupted the chemisorbed layer and some surface silane was produced, but the material produced in this fashion did not exhibit the properties of RS.

Method 5. It was found that if ordinary silica is heated in an atmosphere of SiH_4 at about 250°C, an active silica similar to RS has formed. It is known that SiH_4 will decompose to the elements near 400°C. Apparently the presence of a high surface area silica powder will accelerate the decomposition. The SiH_4-treated silica had several different types of silicon hydride groups on its surface. Also, the SiH_4 decomposition apparently lead to the deposition of some very active material which was probably elemental silicon.

Method 6. This item lumps together a series of experiments which have been unsuccessful. It has not been possible to make RS by forming surface ethoxy groups, propyl groups, methyl groups, etc. It seems, so far, that RS is formed only when a $-OCX_3$ structure is attached to the surface and that structure is then disrupted; structures containing a carbon chain do not seem able to produce RS.

The CCl_4-SiO_2 Interaction

Some spurious effects were observed in the behavior of SiO_2 when the vaccum system contained some traces of CCl_4. A small amount of experimental work was consequently carried out in order to define the role of CCl_4 in modifying SiO_2 surfaces. It was found that surface silanol groups were removed at temperatures above 300^0. Such a dehydroxylated surface could be easily re-hydroxylated by reaction with H_2O at 25^0. The various results are described in a note, M. Shimizu and M.J.D. Low, J. Amer. Ceram. Soc., 54, 271 (1971).

CONCLUSIONS

(a) An entirely new type of surface defect has been discovered. The defect has the properties expected for a center consisting of two closely-spaced silicon radicals associated with two anomalously reactive oxygen atoms.

(b) The defect responsible for the activity of RS is best produced by a methoxylation, pyrolysis, degassing procedure. Materials having some of the properties of RS can be produced by treating silicas with certain silanes.

(c) RS and its reactions provide an extremely interesting and entirely novel aspect of the chemistry of siliceous surfaces.

PUBLICATIONS

One publication dealing with the SiO_2-CCl_4 interaction has appeared and has been submitted as Technical Report.

A paper dealing with the general mechanism of the reactivity of RS has been accepted by the Journal of Catalysis.

A monograph dealing with all aspects of RS, including the topics mentioned in the Progress Reports, has been prepared and submitted to the New York Academy of Sciences.