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Structure of poly(vinylpyrrolidone)-silica hybrid

Motoyuki Toki*, Tak Yuen Chow, Tadao Ohnaka, Hideo Samura, and Takeo Saegusa

Kansai Research Institute, Kyoto Research Park 17, Chudoji Minami-machi, Shimogyo-ku,
Kyoto 600, Japan

Summary

This paper is concerned with the solid structure of a new group of transparent glass materials which consist of an organic polymer and a metal oxide, namely a combination of poly(vinylpyrrolidone) and dry silica gel. The structure was analyzed by Atomic Force Microscopy (AFM), BET analysis method, and CP MAS ^{13}C-NMR. BET measurement showed that the hybrid material had a quite dense structure which was much less porous than the reference dry silica gel prepared by the conventional sol-gel process. AFM analysis gave the same conclusion, i.e., it showed a granular structure of silica of about 1 nm size. Silica and PVP domains did not show any considerable aggregation. The transparent, homogeneous, and dense structure was attributed to the hydrogen-bond formation between PVP(carbonyl group) and silanol, as demonstrated by CP MAS ^{13}C-NMR spectroscopy.

Introduction

During the past decade there has been an enormous growth in the interest in the sol-gel process, as described in several reviews such as those by Hench1), Scherer2), Johnson3), Rabinovich4), and by Brinker and Scherer5).This growth has been stimulated by the applicability of the sol-gel process to various fields, such as glass6) and ceramic manufacturing, optical7) and electrical devices, and catalyst preparation 8).

One of the important extentions of the sol-gel process is the preparation of a group of transparent glass materials consisting of an organic polymer and a metal oxide such as silica gel. In order to differentiate from so-called "composite", these transparent materials are called "hybrids". Preparation of the hybrid is accomplished easily by the sol-gel process of a metal alkoxide in

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*Corresponding author

the presence of an organic polymer whose repeating units possess an N-alkyl or N,N-dialkylamide group[9-13]. The polymer molecule is dispersed in the three-dimensional network of metal oxide such as silica by means of the formation of hydrogen-bond between the amide carbonyl group of polymer and the silanol group of silica[11,13].

This communication describes the results of the structural analysis of the PVP-silica hybrid which is prepared by the sol-gel process of tetraethoxysilane(TEOS) in the presence of PVP. Analytical methods employed were AFM, BET and CP MAS 13C-NMR.

Experimental

Reagents

Tetraethoxysilane (TEOS) and poly(vinylpyrrolidone) (PVP), ethanol (EtOH), and isopropanol (IPA) as solvent were all of reagent grade which were used as supplied.

Synthesis

PVP-silica hybrid material was prepared by the following process. PVP (60g) was dissolved in IPA (350ml), to which TEOS (104g), IPA (350ml) and 0.05N HCl solution (36ml) were added. The reaction mixture was stirred for 3 hours, followed by evaporation to concentrate the reaction mixture to a half of the original volume. The concentrated viscous mixture was air-dried at room temperature under ambient pressure in an open polypropylene container for 10 days to produce a transparent hybrid material.

A reference sample of dry silica gel was prepared by the conventional sol-gel method. Thus a mixture of TEOS (104g) and 0.05N HCl solution (45ml) was stirred vigorously to produce a homogeneous and transparent viscous solution, to which 0.1N NH_4OH solution was added to adjust pH of the mixture to pH 5.0. The final mixture was air-dried in a polypropylene container at room temperatue for 10 days to produce dry silica gel.

Measurements

The structure of PVP-silica hybrid was subjected to analysis by AFM (NanoScope III SPM System,Digital Instruments,Inc.), BET(Sorptmatic 1800type, Carlo-Erba) and CP MAS ^{13}C NMR (JNM-GSX 270, 270 MHz, JEOL).

Results and discussion

It was reported previously[14)] that dry silica gel prepared by the conventional sol-gel process with acid catalyst was a porous material having micropores in a range from 1.5 to 10 nm and that the apparent density was 1.0 to 1.5. In the present study, the micropore distribution of the reference silica gel was examined (Figure 1).

It is seen in the Figure that a pore radius around 20Å is predominant. The pore characteristics of the reference silica gel have been explained[15-18)] as follows. Primary particles of about 20Å diameter are first formed, which agglomerate to secondary particles of about 60Å diameter and finally to the three-dimensional network of silica gel.

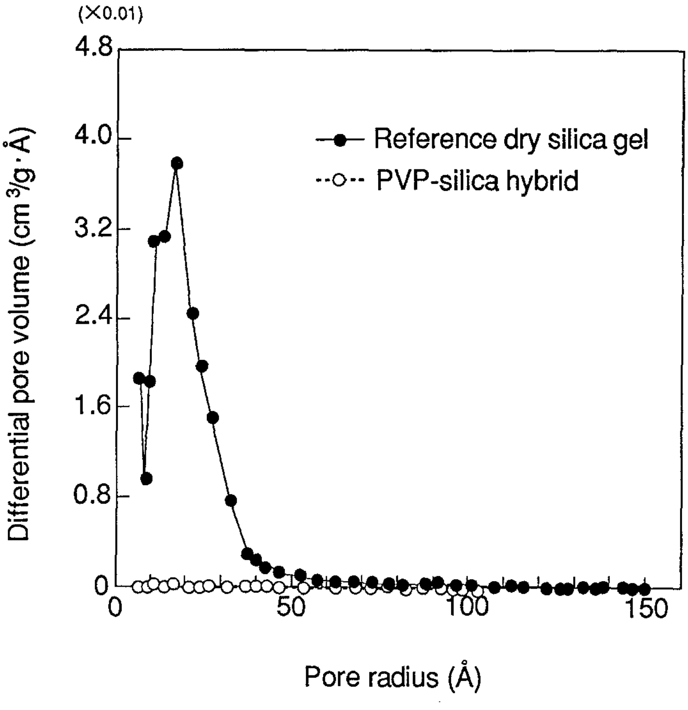

Figure 1. Micropore distribution of reference dry silica gel synthesized by sol-gel method, and PVP-silica hybrid material.

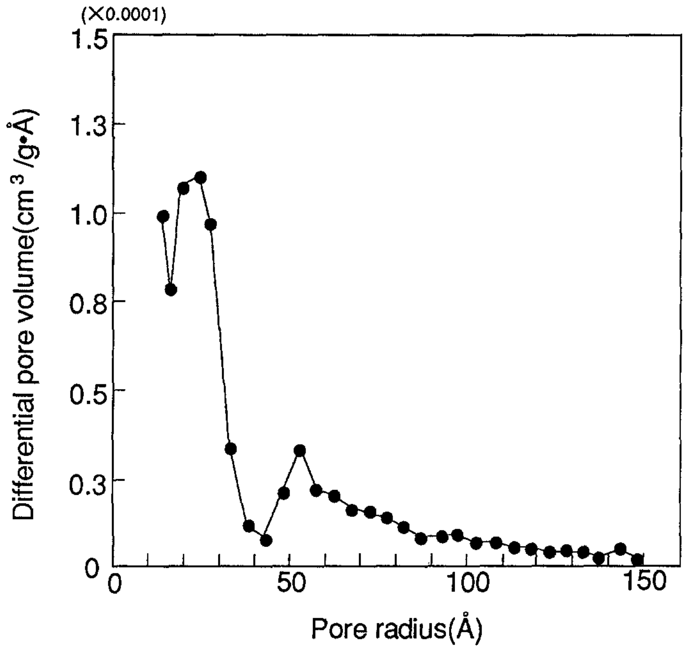

Figure 2. Micropore distribution of 67% PVP-silica hybrid

In the PVP-silica hybrid, on the other hand, there are very little pores (Figure 1). In the magnified curve of pore-distribution (Figure 2), a small amount of pores of 20Å diameter is observed, which is taken to correspond to those of the reference sample. In addition, Table I indicates a comparison of the total surface area and pore volume between the reference silica dry-gel and the hybrid. An extremely dense structure of the hybrid is clearly shown.

Table 1. Comparison of pore volume between dry silica gel and hybrid.

	Specific surface area m^2/g	Pore volume cm^3/g
Silica dry-gel	859	0.659
67%PVP-silica hybrid	1.1	0.003

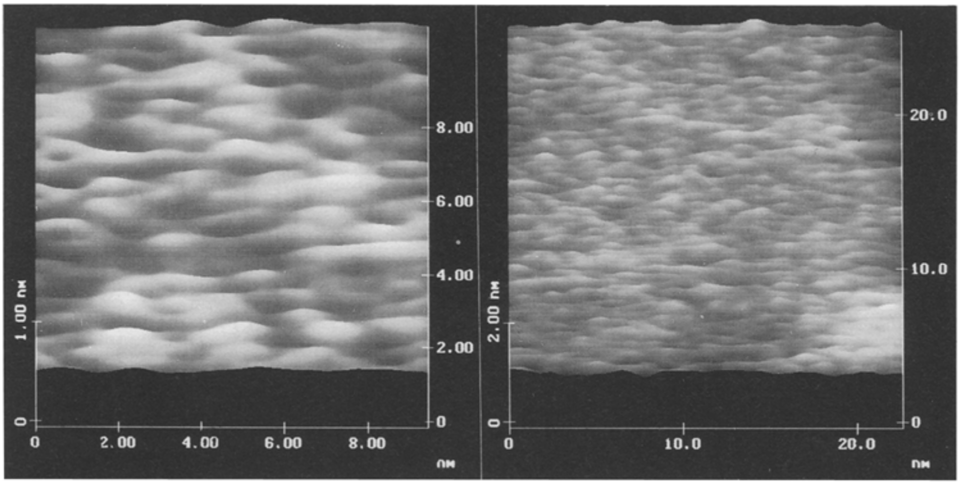

Figure 3. AFM image of PVP-silica hybrid surface.

The dense structure of the hybrid has been supported by AFM analysis (Figure 3), where the primary particles of silica are of about 1nm. In the magnified image at the left portion of Figure 3, a few rings of about 5 to 10 Å are seen in the particles of silica, which may be taken to show the pyrrolidone rings of PVP or rings consisting of 4 silica tetrahedrons. This interpretation of the AFM image is compatible with the pattern of its depth profile (Figure 4).

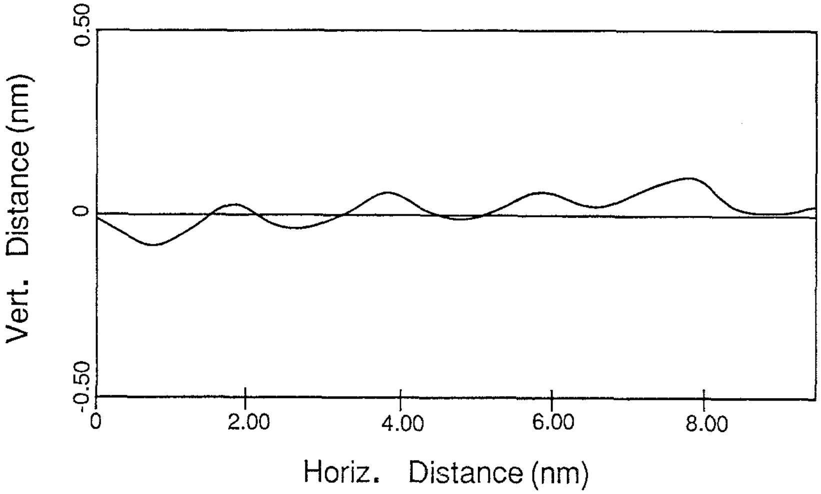

Figure 4. Depth profile of AFM image.

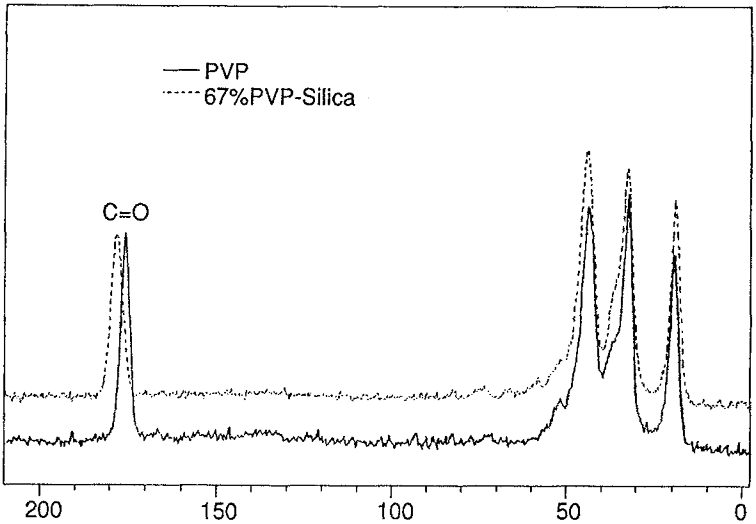

Figure 5. CP MAS ^{13}C NMR spectra of PVP and PVP-silica hybrid material

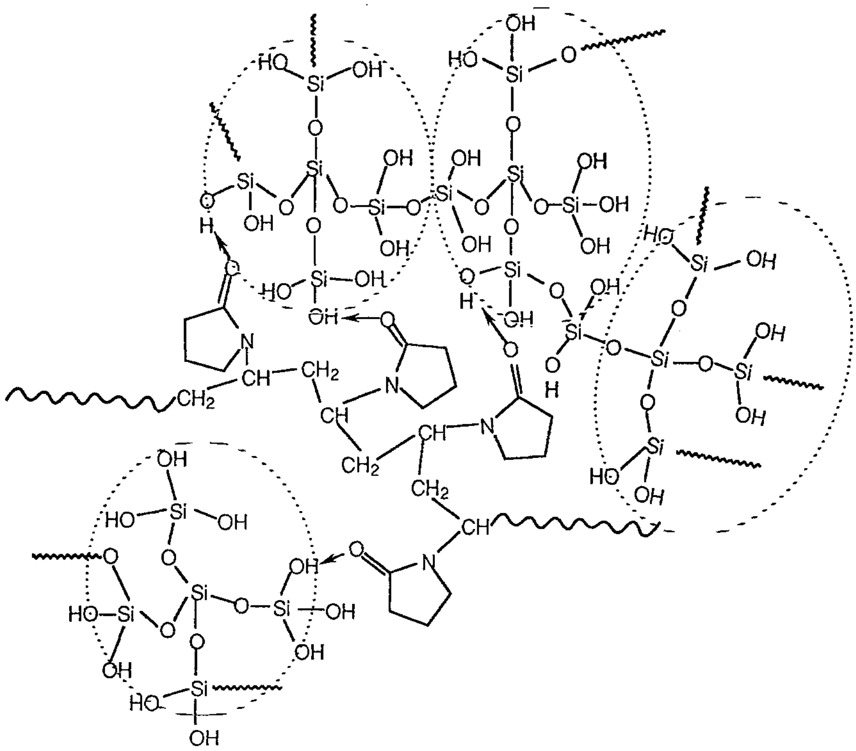

Figure 6. Structure of PVP-silica hybrid material.

CP MAS ^{13}C NMR of the hybrid indicates clearly the formation of hydrogen bond (Figure 5) between silanol and carbonyl of PVP. Thus, a shift of absorption due to the carbonyl carbon atom is observed which is caused by the interaction with silanol group of silica gel. This result is in good agreement with that of pevious papers by one of present authors$^{11,13)}$, in which the shift of $\upsilon_{C=O}$ of the FT-IR spectrum of PVP-silica hybrid was demonstrated.

On the basis of the observations by BET, AFM and CP MAS ^{13}C-NMR, the structure of the hybrid may be illustrated by a schematic expression of Figure 6. Thus, silica gel particles of a size of about 1nm are being linked together and each particle is associated with PVP by hydrogen bonding.

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