

**Organic/ Inorganic
Hybrid Materials**

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PREFACE

In materials science, it is well known that (1) processing and intrinsic materials properties together dictate microstructure, (2) intrinsic materials properties and microstructure together dictate macroscopic properties, and (3) control of processing at finest scales gives the highest homogeneity or controlled heterogeneity and therefore the best control of final properties. In principle, if one can control processing to achieve the highest homogeneity (or controlled heterogeneity), then it should be possible to obtain exceptional control over a material's reproducibility, predictability and tailorability.

In the past thirty years, tremendous investments in time, energy and resources have been made to learn to control materials properties at the atomic scale using chemical processing (e.g. sol-gel) methods. Successes in chemical processing are now being extended to the next length scales (1-1000 nm) to produce nanocomposite or organic/inorganic hybrid materials. Recent exceptional advances in hybrid materials synthesis, characterization and processing suggest that this area will occupy scientists and engineers for at least as long a period, and have prompted us to organize this symposium.

The objective of this 1998 MRS Spring Meeting symposium was to create a forum for researchers involved in the synthesis, characterization, processing and properties analysis of organic/inorganic hybrid materials to share views, learn about the leading-edge science and engineering occurring around the world, and to develop new ideas/points of view for their own research efforts. The symposium was divided into nine focus areas that were reduced to seven for this volume. These focus areas included: molecular (1-2 nm length scales) and nanocomposite (1-1000 nm length scales) hybrid synthesis, processing and characterization; porous materials produced by hybrid processing methods; hybrid materials that exhibit optical, electronic, catalytic or physical properties; and new methods of characterizing these materials.

Initially, almost 150 abstracts were submitted for this symposium. Because of space constraints, we were limited to choosing 116 oral and poster presentations, fifty-three of which are contained in this volume. All of the papers were subject to peer review. After authors responded to the referees' comments and made corrections, all of the papers were accepted (some with minor editing) without further review.

Richard M. Laine
Clément Sanchez
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Emmanuel Giannelis

September 1998

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Part I

Molecularly Designed Hybrid Materials

THE CUBEOCTAMERIC SILICATE ANION: FORMATION AND APPLICATION TO POROUS MATERIAL SYNTHESIS

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ABSTRACT

The cubeoctameric silicate anion is one of compounds which can be used as a building block for constructing nanostructures of materials. This paper deals with the synthesis and reactivity of the silicate anion and organic-inorganic hybrid and inorganic multi-component porous materials produced from the anion.

INTRODUCTION

The cubeoctameric silicate anion ($\text{Si}_8\text{O}_{20}^{8-}$) is one of inorganic compounds that can easily be synthesized [1,2], although the anion can also be found in natural silicate minerals, for example, ekanite [3]. In recent years, the anion has been attracting much attention as a building block for molecularly designed materials.

The structure of $\text{Si}_8\text{O}_{20}^{8-}$ corresponds to the D4R secondary building unit of zeolites [4]. Then, many efforts have been made to produce porous materials from the silicate anion or compounds with the silicate structure. There have appeared papers on SiO_2 xerogels [5], P(III)-containing silicate [6], organic- SiO_2 hybrids [7-13], Si-C-O ceramics [14], and SiO_2 - ZrO_2 powders [15] with high surface areas, which were produced from the anion or the compounds.

This paper deals with the synthesis of tetramethylammonium [$\text{N}^+(\text{CH}_3)_4$, TMA] silicate and (2-hydroxyethyl)trimethylammonium [$\text{N}^+(\text{CH}_3)_3(\text{C}_2\text{H}_4\text{OH})$, choline] silicate, which have the $\text{Si}_8\text{O}_{20}^{8-}$ structure in their silicate skeletons, and some of their reactions. TMA silicate is obtained as a methanolic solution and choline silicate as a solid. We have so far attempted the building block approach to organic-inorganic porous hybrids using TMA silicate [10-13] and inorganic multi-component porous materials using choline silicate [15], which are also described.

TMA SILICATE

The $\text{Si}_8\text{O}_{20}^{8-}$ silicate anion was synthesized using TMA ions by Hoebbel and Wicker for the first time [16]. The formula of the compound was shown as $\text{Si}_8\text{O}_{20}[\text{N}(\text{CH}_3)_4]_8 \cdot \sim 69\text{H}_2\text{O}$. The crystal structure of $\text{Si}_8\text{O}_{20}(\text{OH})_4[\text{N}(\text{CH}_3)_4]_{16} \cdot 116\text{H}_2\text{O}$ was determined by X-ray crystallography [17]. Following the discovery of $\text{Si}_8\text{O}_{20}[\text{N}(\text{CH}_3)_4]_8 \cdot \sim 69\text{H}_2\text{O}$, investigations were made on distribution of silicate species in aqueous solutions of TMA silicate in order to clarify the composition of the solutions where $\text{Si}_8\text{O}_{20}^{8-}$ is dominantly present [18-20]. In the aqueous solutions at low SiO_2 concentrations, low-molecular silicate species, such as the monomer (SiO_4^{4-}) and dimer ($\text{Si}_2\text{O}_7^{6-}$), are main components. With an increase in the SiO_2 concentration, polymerization of the silicate species takes place and the $\text{Si}_8\text{O}_{20}^{8-}$ species is formed at the expense of the low-molecular silicate species. When the TMA ion-to- SiO_2 molar ratio of the solutions is kept constant at 1.0, the silicate species dominates in the solutions at SiO_2 concentrations over 0.7 mol dm^{-3} [20]. {These solutions were prepared with tetraethoxysilane [$\text{Si}(\text{OC}_2\text{H}_5)_4$, TEOS] as a SiO_2 source.} The trimethylsilyl derivative of the species,

$\text{Si}_8\text{O}_{20}[\text{Si}(\text{CH}_3)_3]_8$, can be obtained at yields over 50% from the solutions by trimethylsilylation method of Lentz [21].

The aqueous solution of TMA silicate is a useful source, for example, for preparing a variety of silyl derivatives of the $\text{Si}_8\text{O}_{20}^{4-}$ silicate anion, since cost-effective polymeric SiO_2 sources, such as SiO_2 gels, can be used for the preparation, although it takes longer times for the solutions prepared with polymeric SiO_2 sources to attain the equilibrium where the $\text{Si}_8\text{O}_{20}^{4-}$ species is present dominantly [23]. The problem with the solution, however, is that a small amount of the monomer is usually present together with $\text{Si}_8\text{O}_{20}^{4-}$. When a reaction of $\text{Si}_8\text{O}_{20}^{4-}$ is carried out using the aqueous solution, the monomer gives by-products which are, in some cases, difficult to remove.

On the other hand, the methanolic solution of TMA silicate gives $\text{Si}_8\text{O}_{20}^{4-}$ solely upon adjusting the composition of the solution [23,24]. Figure 1 shows the ^{29}Si NMR spectrum of a methanolic solution of TMA silicate at a SiO_2 concentration of 1.0 mol dm^{-3} , a TMA hydroxide concentration of 1.0 mol dm^{-3} , and a H_2O concentration of 10.0 mol dm^{-3} . The preparation procedure has been described in detail [25]. The spectrum gives rise to only one signal at -99.2 ppm which is assigned to the $\text{Q}^3 [\text{Si}(\text{OSi})_3(\text{O})^-]$ unit in $\text{Si}_8\text{O}_{20}^{4-}$ [24]. Trimethylsilylation of the solution by the Lentz method gives $\text{Si}_8\text{O}_{20}[\text{Si}(\text{CH}_3)_3]_8$ at a yield of 90% [23]. No trimethylsilyl derivatives of low-molecular silicate species are obtained.

It should be noted that the addition of H_2O to the solution is necessary for the formation of $\text{Si}_8\text{O}_{20}^{4-}$ [23]. The H_2O , however, makes problems. When $\text{Si}_8\text{O}_{20}^{4-}$ in the methanolic solution is allowed for a reaction with trimethylchlorosilane $[(\text{CH}_3)_3\text{SiCl}]$, TMCS using THF as solvent for the synthesis of $\text{Si}_8\text{O}_{20}[\text{Si}(\text{CH}_3)_3]_8$, for example, a large amount of TMCS has to be used to obtain $\text{Si}_8\text{O}_{20}[\text{Si}(\text{CH}_3)_3]_8$ at a high yield [26]. This results from the fact that TMCS reacts with H_2O in the methanolic solution to give hexamethyldisiloxane $[(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3]$. As a result, the reaction of TMCS with $\text{Si}_8\text{O}_{20}^{4-}$ does not proceed efficiently, resulting in the formation of incompletely trimethylsilylated derivatives of $\text{Si}_8\text{O}_{20}^{4-}$, $\text{Si}_8\text{O}_{20}[\text{Si}(\text{CH}_3)_3]_{8-n}(\text{H})_n$ ($n = 1-3$) and, therefore, a low yield of $\text{Si}_8\text{O}_{20}[\text{Si}(\text{CH}_3)_3]_8$.

One of methods to avoid the effect of H_2O is to use 2,2-dimethoxypropane (DMOP) as solvent [26]. Since DMOP hydrolyzes to form acetone and methanol, the effect of H_2O can be suppressed, leading to the formation of $\text{Si}_8\text{O}_{20}[\text{Si}(\text{CH}_3)_3]_8$ at a high yield even if the amount of TMCS used for the reaction is small. Figure 2 shows the variation in the yield of $\text{Si}_8\text{O}_{20}[\text{Si}(\text{CH}_3)_3]_8$ produced by the reaction of $\text{Si}_8\text{O}_{20}^{4-}$ in the methanolic solution with TMCS using THF or DMOP as solvent as a function of TMCS-to-Si in $\text{Si}_8\text{O}_{20}^{4-}$ molar (TMCS/Si) ratio.

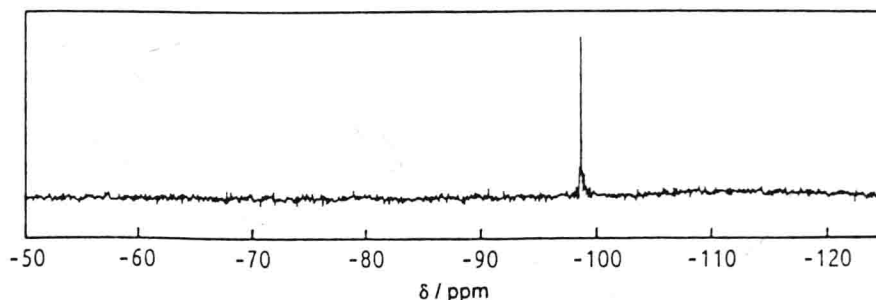


Figure 1. The ^{29}Si NMR spectrum of the methanolic solution of TMA silicate at a SiO_2 concentration of 1.0 mol dm^{-3} , a TMA hydroxide concentration of 1.0 mol dm^{-3} , and a H_2O concentration of 10.0 mol dm^{-3} .

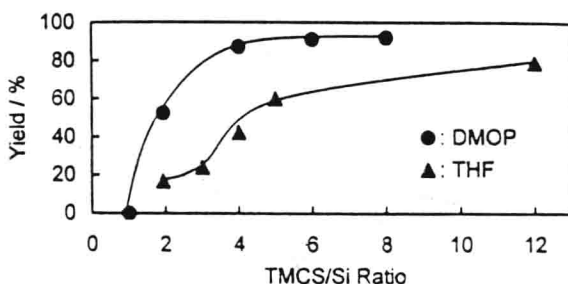


Figure 2. Variation in the yield of $\text{Si}_4\text{O}_{20}[\text{Si}(\text{CH}_3)_3]_8$ formed by the reaction of $\text{Si}_4\text{O}_{20}^{4-}$ in the methanolic solution of TMA silicate with TMCS using THF or DMOP as solvent as a function of the TMCS/Si ratio. The yield was measured with gas-liquid chromatography.

Organic-Inorganic Porous Hybrids Produced with TMA Silicate

As described above, the reaction of $\text{Si}_4\text{O}_{20}^{4-}$ with TMCS can be carried out efficiently by using DMOP as solvent. In addition, the formation of $\text{Si}_4\text{O}_{20}[\text{Si}(\text{CH}_3)_3]_8$ at a high yield means that no breakdown of the $\text{Si}_4\text{O}_{20}^{4-}$ structure takes place during the reaction. Then, it is anticipated that the reaction of $\text{Si}_4\text{O}_{20}^{4-}$ with diorganodichlorosilane in DMOP gives organic-inorganic hybrids which consists of the $\text{Si}_4\text{O}_{20}^{4-}$ structure as a building block.

The reaction of $\text{Si}_4\text{O}_{20}^{4-}$ in the methanolic solution with dimethyldichlorosilane $[(\text{CH}_3)_2\text{SiCl}_2, \text{DMDCS}]$ in DMOP was carried at room temperature for 1 h. The detailed procedure has been described in Refs. 10 and 11. Figure 3 (a) shows the ^{29}Si CP/MAS NMR spectra of the products obtained by the reaction at a DMDCS-to-Si in $\text{Si}_4\text{O}_{20}^{4-}$ (DMDCS/Si) ratio of 1.0. There appear signals from four different siloxane units, that is, D^1 $[(\text{CH}_3)_2\text{Si}(\text{OSi})(\text{O})]$, -8.5 ppm], D^2 $[(\text{CH}_3)_2\text{Si}(\text{OSi})_2]$, -16.5 ppm], Q^3 (-100.1 ppm), and Q^4 $[\text{Si}(\text{OSi})_4]$, -109.1 ppm] units.

In the ^{29}Si NMR spectrum of a mixture of $\text{Si}_4\text{O}_{20}[\text{Si}(\text{CH}_3)_3]_{2n}(\text{H})_n$ ($n = 0-2$), the Q^3 units in the compounds give rise to signals in the range of -100.0 and -100.4 ppm and the Q^4 units in the range of -108.5 and -109.2 ppm [26]. From the chemical shift values of the Q^3 and Q^4 signals in Fig. 3 (a), it is inferred that these signals would result from the Q^3 and Q^4 units involved in the cubeoctameric silicate unit.

The chemical shift value of the D^2 signal is *ca.* 4 ppm higher than those of signals due to D^2 units in polydimethylsiloxanes (-20 - -23 ppm) [27]. The shift has been demonstrated to result from the replacement of the D unit adjacent to a D^2 unit by the Q unit [28,29]. The FT-IR spectrum of the product gives rise to two sharp bands at 804 and 850 cm^{-1} , which are assigned to the $\text{Si}(\text{CH}_3)_2$ stretching vibrations of the D unit connecting to the Q unit [28,29]. These indicate the presence of the D-Q linkage in the product, and thus it would be stated that the product is a hybrid consisting of the $\text{Si}_4\text{O}_{20}^{4-}$ core as a building block which is linked by the $\text{Si}(\text{CH}_3)_2$ group.

The hybrid reveals a BET surface area of 31 $\text{m}^2 \text{g}^{-1}$. The area increases to 339 $\text{m}^2 \text{g}^{-1}$ upon heating at 350 $^\circ\text{C}$ in air for 1 h. The solid-state ^{29}Si NMR spectrum of the hybrid after the heat-treatment is shown in Fig. 3 (b). Comparing with Fig. 3 (a), it is seen that the D^1 signal almost disappears and instead the D^2 signal increases in intensity, suggesting condensation of the D^1 unit took place during the heat-treatment. On the other hand, two new signals appear at -52.7 and -64.6 ppm, which are ascribable to the T^2 $[(\text{CH}_3)_2\text{Si}(\text{OSi})_2(\text{O})]$ and T^3 $[(\text{CH}_3)_2\text{Si}(\text{OSi})_3]$ unit, respectively. The formation of the units would imply that a part of D units in the hybrids is

oxidized during the heat-treatment. Nevertheless, the D^2 signal appears at -15.6 ppm and the Q^4 signal at -108.3 ppm, indicating the D-Q linkage and the $Si_8O_{20}^{8-}$ core in the hybrids are preserved during the treatment.

The pore size distribution of the hybrid after the heat-treatment, plotted by BJH method from the adsorption isotherm, is shown in Fig. 4. (Since its adsorption and desorption isotherms were not reversible, the pore size distribution was tentatively measured from the adsorption isotherm.) There appears a peak in the distribution. Despite the problem with the measurement, this would indicate that the hybrid subjected to the heat-treatment is porous.

In the DTA-TG curve of the product, exothermal reactions accompanying weight loss take place at two ranges, 245-295 and 345-636 °C. Bands due to the C-H and CH_3 -Si vibrations disappear in the FT-IR spectrum of the product formed by heating the hybrid at 800 °C in air. Thus, the exothermal reaction occurring at 345-636 °C is attributed to thermal decomposition of the CH_3 -Si bond. On heating the hybrid at 450 °C in air for 1 h, the surface area decreases to 247 $m^2 g^{-1}$ and the area becomes below 5 $m^2 g^{-1}$ by the treatment above 600 °C. The decrease in the surface area is attributed to collapse of the nanostructure of the hybrids led by the thermal decomposition of the CH_3 -Si bond. These indicate that the heat-treatment at 350 °C is effective for producing the hybrid with a higher surface area, although a portion of D units in the hybrid degrades.

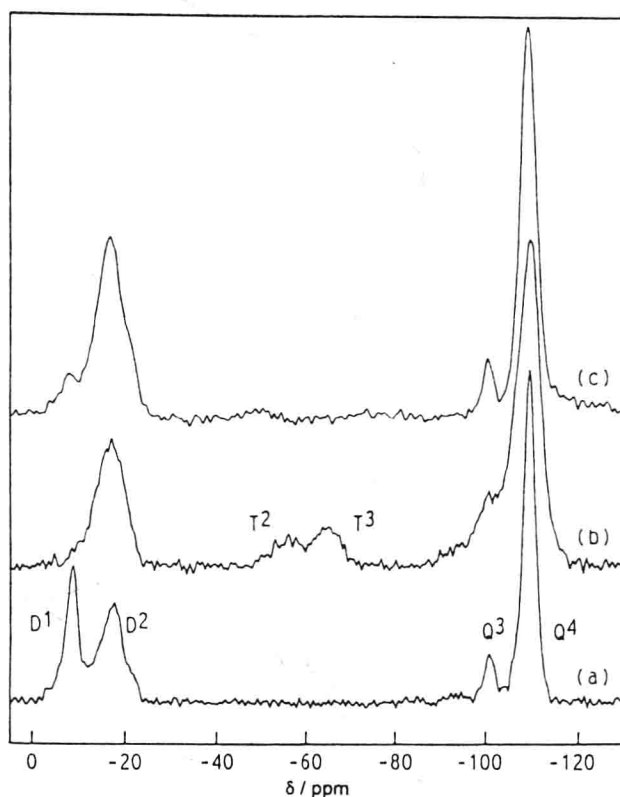


Figure 3. The ^{29}Si CP/MAS NMR spectra of (a) the organic- SiO_2 hybrid formed by the reaction of $Si_8O_{20}^{8-}$ with DMDCS at a DMDCS/Si ratio of 1.0, (b) the hybrid subjected to the heat-treatment at 350 °C in air for 1 h, and (c) the hybrid subjected to the hydrolysis treatment.