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Editor's Choice

Simple and Rapid Eco-friendly Synthesis of Cubic Octamethylsilsesquioxane Using Microwave Irradiation

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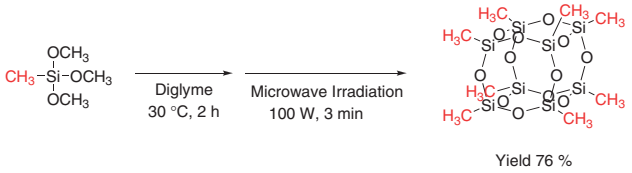
Octamethylsilsesquioxane ($Me_8Si_8O_{12}$) having a cage structure was rapidly prepared by means of microwave-assisted sol–gel reaction of methyltrimethoxysilane as a trifunctional alkoxysilane with an aqueous basic solution in diglyme as a solvent. Moreover, octamethylsilsesquioxane was obtained as cubic particles in a good yield. Cubic octamethylsilsesquioxane could be formed under microwave irradiation owing to the formation of micelles which are organized by eight methyltrimethoxysilane molecules in diglyme.

Silsesquioxane chemistry has been the subject of intense interest for more than half a century.[1–8] The term silsesquioxane is the general name for organosiloxide species with an empirical formula $(RSiO_{1.5})_n$ (R = H, hydrocarbon) and closely related compounds. In particular, silsesquioxane structures, which are random, ladder, cage (cubic), or partial cage, are interesting.[9] Since the caged part of silsesquioxane has a structure similar to silica gel, these compounds can be regarded as a model of inorganic compounds. Silsesquioxane and its derivatives have a wide range of potential applications. In recent years, the polyhedral oligomeric silsesquioxanes (POSS) have been attracting a great deal of attention. However, a long reaction time is usually required to obtain silsesquioxanes. Moreover, the yields of silsesquioxanes are not so high in general. Due to increasing environmental concern, green chemistry has been receiving progressively more attention since the 1990s.[10–12] Therefore, there is a great necessity for the advancement of novel methodologies for chemical reactions using an environmentally eco-friendly method. A promising approach from this standpoint would be to search for new processes and technologies which from the very beginning are aimed at sharply curtailing environmental pollution by reducing the volumes of chemical production wastes. Microwave irradiation has been applied to various chemical reactions. Many review papers have been published about microwave-assisted chemical reactions.[13–16] The microwave method provides fast and direct heating. In many cases, it can dramatically reduce the reaction time from hours to minutes, and would increase the product yields and enhance the product purity. For example, the monodisperse submicrometer silica spheres were prepared rapidly by the microwave-assisted sol–gel reaction of tetramethoxysilane.[17] Silica mixed oxide such as Mg_2SiO_4,[18] and organic polymer–silica hybrid[19] were also synthesized using microwave-assisted sol–gel reaction. In this study, we tried to overcome the difficulties in synthesis of silsesquioxanes, using microwave irradiation (Scheme 1).

To find suitable reaction conditions, experiments were carried out using different catalysts. As a preliminary experiment, the reactions of methyltrimethoxysilane (MeTMOS) with various sol–gel reaction catalysts (0.1 M LiOH aq., 0.1 M NaOH aq., or 0.1 M KOH aq.) were carried out in a PTFE beaker in a microwave oven. Into a 50-mL glass bottle, diglyme (40 mL) was added followed by addition of MeTMOS (1.00 g) and sol–gel reaction catalysts (0.5 mL). For the hydrolysis of MeTMOS, the mixture was stirred at ambient temperature for 2 h. The solution was then poured into a PTFE beaker. The beaker was placed at the center of the microwave oven and the solution was irradiated at 100 W for 3 min. After microwave irradiation, the reaction mixture changed to a suspension, except for the use of LiOH as a catalyst (Table 1, Runs 1–3). To evaluate the effect of catalyst concentration, the experiments were carried out in 1.0 M catalyst solution. In the case of KOH (Run 6), the precipitate product was obtained in a good yield. The yield of the product increased in order of KOH > NaOH > LiOH (Table 1, Runs 4–6). In the case of Run 6, the suspension was not obtained by the microwave irradiation without stirring at room temperature for 2 h. Also the suspension was not obtained by the sol–gel reaction without the microwave irradiation.



Scheme 1. Synthesis of octamethylsilsesquioxane using microwave irradiation.

Table 1. Sol–gel reaction of MeTMOS under microwave irradiation (100 W)[a]

Run	Catalyst		Yield/%
	Base	Conc./M	
1	LiOH	0.1	0
2	NaOH	0.1	20
3	KOH	0.1	23
4	LiOH	1.0	2
5	NaOH	1.0	52
6	KOH	1.0	76

[a]Conditions: MeTMOS 1.00 g, catalyst 0.5 mL, and diglyme 40 mL.

In the case of Run 6, the precipitates obtained were observed by scanning electron microscope (SEM) measurements. Figure 1 shows the SEM image of the obtained precipitates. The observed particles were sharply cubic particles. The range of particle size was from 0.6 to 3.5 μm.

The obtained particles were examined by XRD analysis.[24] The XRD patterns of the cubic particles agreed with the patterns of the authentic sample and also the reported data.[20] These results suggest that the microwave irradiation gave a cubic octamethylsilsesquioxane. As compared with an authentic sample, the cubic particles had good crystallinity from the

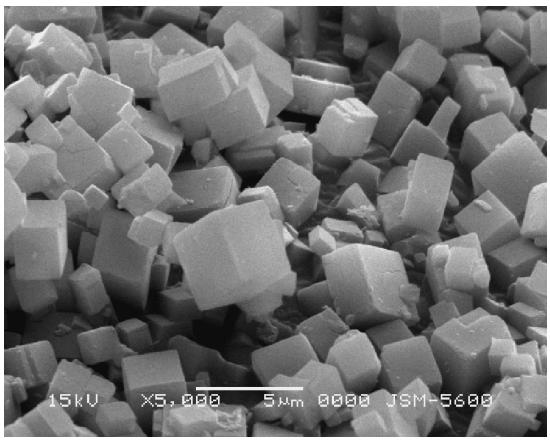


Figure 1. SEM image of the particles obtained by microwave irradiation.

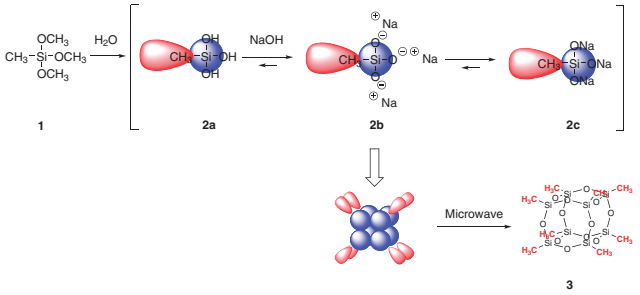
full-width at half maximum (FWHM) of XRD peak at about 10.6° (cubic particles: 0.119°, authentic sample: 0.152°). These results may indicate that this compound has high symmetry.

Gorsh et al. reported that the ^{29}Si NMR spectrum of octamethylsilsesquioxane has two well-resolved lines with an intensity ratio of 3:1 at −66.1 and −66.8 ppm, respectively.[21] For octamethylsilsesquioxane, the distortion of the silicon–oxygen framework along the body diagonal is 0.06 Å.[22] This distortion corresponds to a splitting of 0.7 ppm of the signal in the ^{29}Si NMR spectrum for octamethylsilsesquioxane. In the ^{29}Si NMR spectrum of octamethylsilsesquioxane which was prepared by microwave irradiation, the peak was observed at −66.2 ppm. Therefore, the ^{29}Si NMR spectrum suggests that the cage silsesquioxane obtained by microwave irradiation has high symmetry. Moreover, the ^{29}Si NMR spectrum supported the result of XRD analysis.

The FT-IR spectrum of the obtained cubic particles was in good agreement with the spectrum of octamethylsilsesquioxane.[24] The obtained cubic particles have IR absorptions at 2972 cm^{-1} (asymmetric CH_3 stretch), 1271 cm^{-1} (Si–CH_3 stretch), 1124 cm^{-1} (Si–O–Si), and 773 cm^{-1} (Si–CH_3 due to methyl rocking and Si–C stretching).[23] In this spectrum, an absorption at around 3500 cm^{-1} was observed. This absorption could not be distinguished between the absorption of Si–OH derived from the obtained cubic particles and the absorption of KBr containing H_2O. Since the FT-IR measurement of the cubic particles was carried out in nujol, the absorption at around 3500 cm^{-1} was not observed; this absorption resulted from KBr which included H_2O. Consequently, it was clarified that the obtained silsesquioxane has a complete cage structure.

Also, as a result of the elemental analysis for the obtained silsesquioxane, the measured values of C, 17.84 and H, 4.44% were obtained, wherein the evaluated values for the product were C, 17.89 and H, 4.51%. Therefore, it was also clarified from the elemental analysis that the obtained silsesquioxane has a complete cage structure.

We surmised the formation mechanism of octamethylsilsesquioxane as depicted in Scheme 2. In the first step, silanol **2a** might be generated from MeTMOS (**1**) by H_2O. In this system, there might be equilibrium among **2a**, **2b**, and **2c**. These silanol derivatives could form the micelles which were organized by eight silanol derivatives molecules (**2a**, **2b**, and **2c**) in diglyme. Therefore, octamethylsilsesquioxane (**3**) generated under microwave irradiation would result from the formation of micelles.



Scheme 2. Plausible mechanism for octamethylsilsesquioxane obtained by microwave irradiation.

In summary, cubic octamethylsilsesquioxane ($Me_8Si_8O_{12}$) was rapidly prepared under microwave irradiation by the sol–gel reaction of methyltrimethoxysilane with an aqueous basic solution in diglyme as a solvent. Moreover, cubic octamethylsilsesquioxane was obtained as sharply cubic particles in a good yield (76%). Under the microwave irradiation conditions, cubic octamethylsilsesquioxane could be formed owing to the formation of micelles which are organized by eight methyltrimethoxysilane molecules in diglyme. Silsesquioxane and its derivatives have a wide range of potential applications, for example, coating, adhesion, catalysts, liquid crystalline polymers, hybrid materials, and low dielectric constant materials. Since there is an expectation to use silsesquioxanes in various fields, our eco-friendly method should make it simple to synthesize them.

References and Notes

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