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Effect of Surfactant Concentration on the Physico-chemical characteristics of Mesoporous Molecular Sieve

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Abstract: A series of mesoporous molecular sieve samples have been synthesized hydrothermally by using cetyltrimethylammonium bromide (CTAB) as a template, tetraethyl orthosilicate (TEOS) as a silica source, tetramethyl ammonium hydroxide as a base source and water as a solvent. The samples were prepared by adding required amount of surfactant, TEOS, water and TMAOH to maintain pH, then the obtained mixture was stirred for 10 min. and then transferred into autoclave. pH of the gel was adjusted to 10. The molar ratio of surfactant (CTAB) and TEOS was kept at 0.11:0.48, 0.165:0.48, 0.22:0.48 and 0.274:0.48 for samples A-I, A-II, A-III and A-IV respectively, while the aging time was kept 4 days and temperature remained constant at 393 K. The as-synthesized samples were thoroughly washed with distilled water and then dried at 373 K for 24 h. The as-synthesized samples were calcined at 723 K for 6 h in air. The as synthesized samples were characterized for its morphology using Field Emission Scanning Electron Microscopy (FESEM), elemental analysis by using Energy Dispersive X-Ray (EDX), thermal stability by using Thermogravimetric Analysis (TGA), the functional groups within the samples before and after calcination was analyzed using Fourier Transform Infrared Spectroscopy (FTIR). Formation of the mesoporous material depends on the surfactant, which act as a structure directing agent. Micelles of the surfactant arrange themselves and interact with the silicate ions to form the mesoporous material. In this study, the effect of concentration was studied on the synthesis and found that due to increase in concentration of surfactant, more silica polymerized and formation of material increases.

Key words: Mesoporous molecular sieve, MCM-41, hydrothermal, cetyltrimethyl- ammonium bromide (CTAB)

INTRODUCTION

According to the IUPAC system (IUPAC., 1972) porous materials are classified into three classes; (1) microporous (≤2 nm), (2) mesoporous (~2-50 nm) and (3) macroporous (<50 nm). A major subclass of microporous and mesoporous materials is molecular sieves. Zeolites are the example of microporous materials, in which the micropores are regular arrays of uniformly sized channels, having the largest pore dimensions so far are ~10-12 Å (Meier and Olson, 1992; Szostak, 1989). Due to limited pore dimensions of zeolites, researchers were busy to synthesize materials of mesoporous range. Different materials were synthesized near by the range of mesopores, but in 1992, researchers of Mobil corporation succeeded to synthesize a new family of mesoporous materials M41S. This new family of mesoporous materials is grouped into four main categories i.e., (1) MCM-41, having hexagonal structure MCM-50, having lamellar structure and (4) Molecular organic octomer. MCM-41 and MCM-48 were found to be thermally stable, while MCM-50 and octomer were found thermally unstable. The unique pore dimensions and high surface area of these mesophases represent them as the excellent porous solids. From the two crystalline forms of the M41S family, i.e., hexagonal MCM-41 and cubic MCM-48, the former has attracted considerable attention because of its possible industrial applicability as well as scientific interest. MCM-41 is one of the most extensively studied among the numerous mesoporous materials because of its structural simplicity and ease in preparation. The prestigious features of MCM-41 and in general of most periodic mesoporous materials, are as follows: well-defined pore shapes (hexagonal/cylindrical); narrow distribution of pore sizes; negligible pore networking or pore blocking effects; very high degree of pore ordering over micrometer length scales; tailoring and fine-tuning of pore dimensions (1.5-10 nm) large pore volumes (> 0.6 $cm^3\ g^{-1}$); very high surface area (~700-1500 $m^2\ g^{-1}$); large amount of hydroxyl (silanol) groups (~40-60%); high

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surface reactivity; ease of modification of surface properties and excellent thermal, hydrothermal, chemical and mechanical stability. Due to above-mentioned properties of materials, it is used for a number of applications such as adsorption and separation, ion exchange, catalysis and molecular hosts (Selvam *et al*., 2001).

Mesoporous materials are formed by liquid crystal templating (LCT) mechanism, in which liquid crystals serve as templates and the silicate material forms inorganic walls between the ordered surfactant micelles. The pore diameter can be controlled by using suitable surfactants, adding an auxiliary organic chemical and changing reaction parameters (Kresge *et al*., 1992; Beck *et al*., 1992). The surfactants act as structure directing agents or templating agents for the formation of mesoporous molecular sieve frame work. The best quality of Silica MCM-41 synthesized in the presence of alkyltrimethylammonium bromide (ATAB) surfactants having 12-16 carbon atoms alkyl chains (Beck *et al*., 1994). Heavier surfactants were rarely used because they are difficult to dissolve and surfactants having low molecular weight seem to be more difficult to self organize, thus leading to less ordered materials with broader pore size distributions. The effect of chain length of alkyltrimethylammonium bromide and temperature effect on the synthesis of mesoporous molecular sieve were studied and observed that surfactant with shortest chain length ($n = 6$), gives amorphous or microporous zeolitic materials such as ZSM-5 at the temperature range of 100-200 °C. As the surfactant chain length was increased ($n = 8$, 10, 12, 14 and 16) at 100°C, the formation of mesoporous molecular sieves (MCM-41) was observed. In these cases, a combination of surfactant chain length and reaction conditions favor surfactant aggregation (micelles) and hence supramolecular templates are formed. At synthesis temperatures of 200°C, zeolitic and dense-phase products were obtained for even the higher alkyl chain lengths, suggesting that these supramolecular aggregates were destroyed and molecular structural direction dominated (Beck *et al*., 1994; Sayari and Yang, 2000). For the synthesis of MCM-41, the concentration of surfactant can be as low as, but not below the critical micelle concentration which provides the first direct proof that surfactant micelles act as template for the synthesis. In the absence of the surfactant, the amorphous product obtained and when the surfactant is added, the rate of silicate polymerization increases by a factor of more than 2000. The micelle catalysis mechanism depends on electrostatic interaction at the micelle-silicate interface and the higher silicate concentration near the interface than in the bulk (Cheng *et al*., 1995). Herein we probe the effect of surfactant concentration on the formation of mesoporous molecular sieve at synthesis temperature of 393 K for 4 days.

MATERIALS AND METHODS

Materials: Tetraethylorthosilicate (TEOS) as a Silica source, Hexadecyltrimethylammonium bromide (CTAB) as a surfactant, were purchased from Fluka. Tetramethylammonium hydroxide (TMAOH, 25% solution in water) as a base source to maintain the pH was purchased from Merk and deionized water was used as solvent.

Methods

Synthesis method: Four samples of as synthesized material were prepared hydrothermally with the following molar ratios:

A-I 0.11 CTAB : 0.48 TEOS : 14 H_2O
A-II 0.165 CTAB : 0.48 TEOS : 14 H_2O
A-III 0.22 CTAB : 0.48 TEOS : 14 H_2O
A-IV 0.274 CTAB : 0.48 TEOS : 14 H_2O

TEOS was added to the deionized water in a beaker and CTAB in the deionized water was added in the separate beaker at room temperature. Then both solutions were mixed and stirred for 10 min at room temperature until a clear gel solution was obtained. pH was maintained at 10 by using TMAOH as a base source. Then the gel was transferred into the Teflon-lined stainless steel autoclave and heated (under autogenous pressure) in the oven at 393 K for 4 days. After crystallization, the solid product obtained was filtered, washed with distilled water, dried in air at 393 K and finally calcined at 723 K for 6 h.

Characterization methods: Thermal stability of as-synthesized samples was determined by Thermogravimetric analysis. Thermogravimetry analysis (TGA) was carried out on a Perkin Elmer Pyris 1 thermogravimtric analyzer. The samples were heated in air from 303 to 1173 K at the rate of 20 K min^{-1}. The functional groups within the as-synthesized samples before and after calcinations were analyzed by Fourier Transform Infrared Spectroscopy method. Fourier transform infrared (FTIR) spectra of the samples were recorded at room temperature on a SHIMADZU 8400S spectrometer. The sample was ground by an agate mortar and pestle until it had approximately the same consistency as the KBr. Powder KBr was added, mixed thoroughly and the mixture powder was poured into the sample barrel and pressed at 9000 tons. The FTIR spectrum was obtained over the range between 400-4000 cm^{-1}.

The morphology of as-synthesized samples was determined by Field Emission Scanning Electron Microscopy (FESEM). Field Emission Scanning Electron Microscopy images were recorded on a ZEISS 55 Supra VPFESEM microscope operated at an accelerating voltage of 3.00 kV.

The elemental composition of as-synthesized samples was analyzed by Energy-Dispersive X-ray spectroscopy (EDX) method. EDX spectra were recorded on OXFORD instruments Penta FET precision.

RESULTS

Four samples of as-synthesized mesoporous molecular sieve (A-I, A-II, A-III and A-IV) were synthesized by hydrothermal Process using different concentration of CTAB surfactant.

Thermal properties of as-synthesized samples were investigated by TGA. All four samples showed the same graph in the temperature ranges from 303 to 1173 K. Fig. 1 shows the TGA graph. The graph was divided into three segments of temperature changes relative to weight loss, a) 303 K-423 K, b) 423 K-723 K, c) 723 K-1173 K. Results showed that the weight loss from 303 K- 423 K due to desorption of physically adsorbed water on the mesopores, from 423 K-723 K due to removal of organic template and from 723 K-1173 K due to water loss from the condensation of adjacent Si-OH groups into -Si-O-Si-FTIR analysis was carried out before and after calcinations of the as-synthesized samples. FTIR spectra of as-synthesized samples in transmittance modes are shown in Fig. 2.

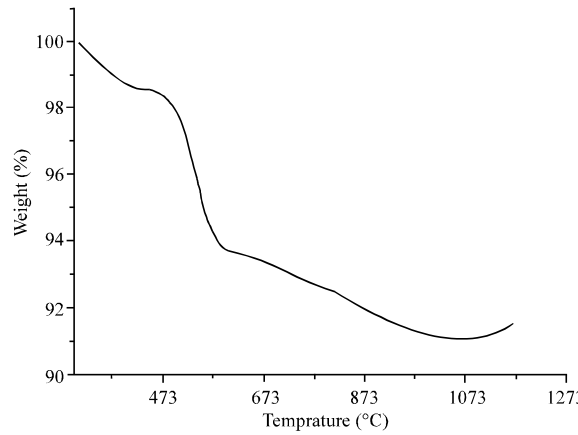

Fig. 1: TGA spectra of as-synthesized material

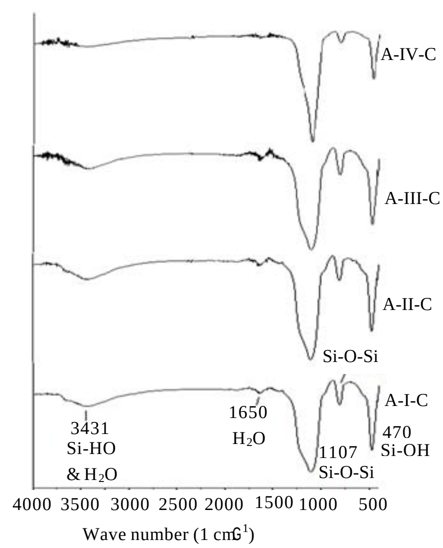

Fig. 2: FTIR spectra of as-synthesized samples (A-I, A-II, A-III and A-IV)

The FTIR results of all samples shows that the broad band at 3,431 cm^{-1} is a characteristic band of Si-OH and water molecules adsorbed; the band at 2920, 2850 and 1477 cm^{-1} are characteristic bands of surfactant alkyl chain ($-CH_2$); the very weak band at 1656 cm^{-1} is associated with the bending mode of H_2O. The spectra in the range of 2500-400 cm^{-1} contain two main bands at ca. 1100 cm^{-1} and 800 cm^{-1} assigned to asymmetric and symmetric stretching of Si-O-Si, respectively. The band at 960 cm^{-1} is assigned to symmetric stretching vibration of Si-O-H groups.

After calcinations, no spectral features were found at 960 cm^{-1} that is a peak from Si-OH, this shows a high degree of polycondensation. The bands at 2,920, 2,850 and 1,477 cm^{-1} disappeared after samples were calcined at 723 k which showed that templates had been removed. FTIR spectra of calcined samples are shown in Fig. 3.

The surface morphology of the as-synthesized samples was studied by Field Emission Scanning Electron Microscopy (FESEM). The FESEM images of as-synthesized products are shown in Fig. 4. Results of FESEM shows that particals in the samples possesses spherical morphology with varied diameter range. In contrast with the spherical morphology, samples also possess irregular shape particals or agglomerates.

Elemental composition of the as-synthesized samples was studied by energy dispersive X-Ray (EDX). EDX graphs of the uncalcined samples are shown in Fig. 5. Results show that all the as-synthesized samples contain silicon, oxygen, along with these elements samples also contain carbon as the surfactant residue and very little amount of Aluminium is present in each sample as impurity.

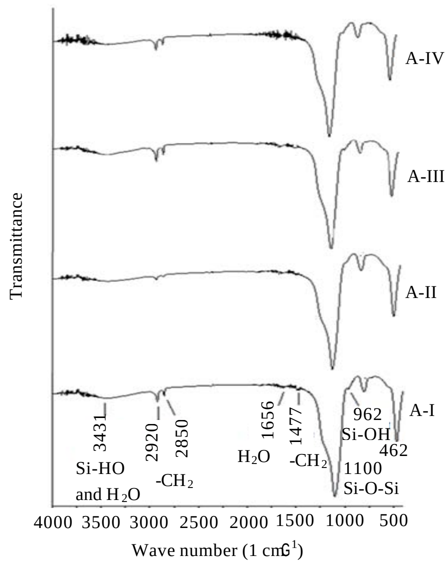

Fig. 3: FTIR spectra calcined samples A-IC, A-IIC, A-IIIC and A-IVC

DISCUSSION

Mesoporous molecular sieve material formed by Liquid Crystal Templating mechanism. In this mechanism liquid crystals serve as templates and the silicate material forms inorganic walls between the ordered surfactant micelles. Two main pathways were proposed for the formation of mesoporous molecular sieve (MMS) as in Fig. 6.

The liquid crystal mesophase or micelles aggregates into rodlike micelles before the addition of the reagents, followed by migration and polymerization of silicate anions resulted in the formation of the MMS structure. Self assembly of the liquid-crystal-like structures as a result of the mutual interactions between the silicate anions and the surfactant cations in the solution, i.e., the silicate species generated in the reaction mixture influence the ordering of the surfactant micelles to the desired liquid-crystal phase (Beck *et al*., 1992; Chen *et al*., 1993).

According to the second pathway, the formation of mesoporous molecular sieve due to the mutual interaction of surfactant cations and silicate anions, this phenomenon was also observed when different concentrations of surfactant were used to analyze the effect on the synthesis of mesoporous material. In sample A-I molar ratio of surfactant and silica source was kept at 0.11 CTAB: 0.48 TEOS and material was formed, but due

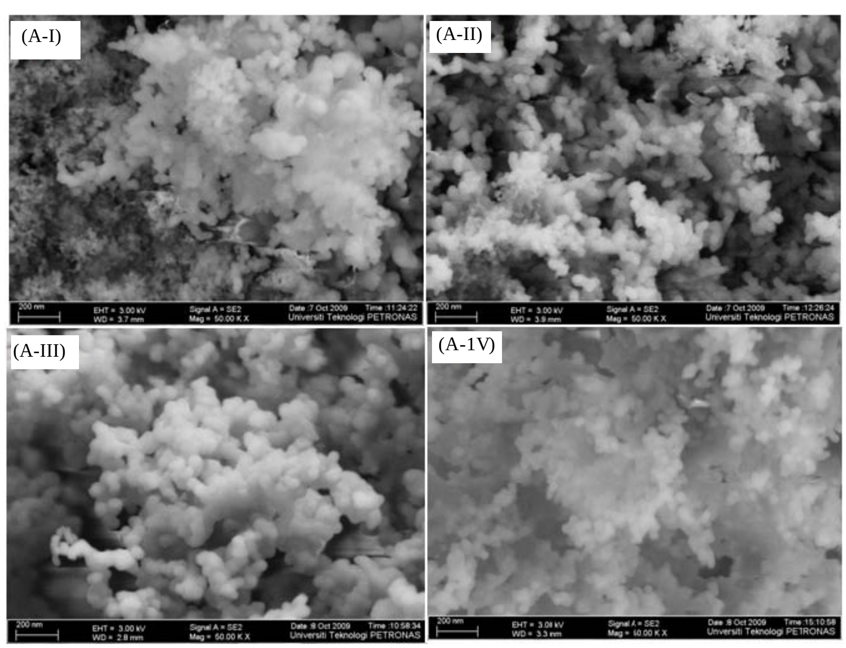

Fig. 4: Field emission scanning electron micrographs of as synthesized samples (a) A-I, (b) A-II, (c) A-III and (d) A-IV

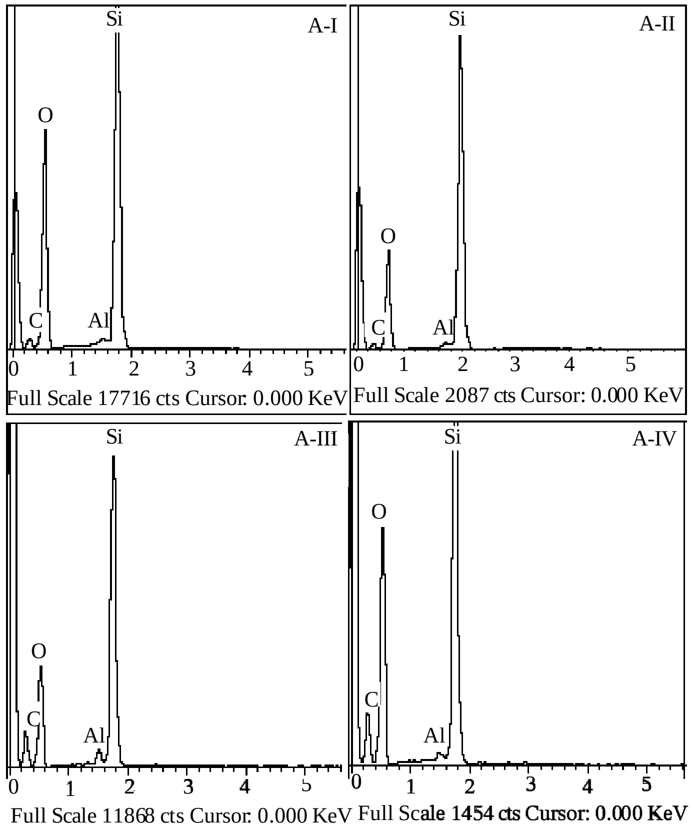

Fig. 5: EDX analysis for A-I, A-II, A-III and A-IV of as-synthesized materia

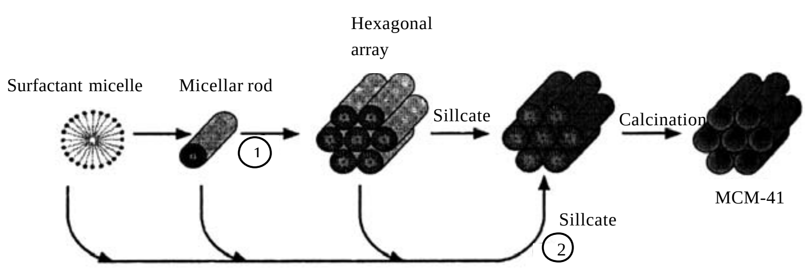

Fig. 6: Possible pathways for the formation of MMS; (1) liquid crystal phase initiated and (2) Silicate anion initiated (Beck *et al*., 1992)

to lesser concentration of surfactant, the gel formation observed was lesser. In sample A-II, concentration of surfactant increases so that molar ratio become 0.165 CTAB:0.48 TEOS. It was observed that an increase in concentration of surfactant resulted in more interaction of surfactant cations with silicate anions, thus more gel material was formed. In sample A-III the surfactant concentration has been further increased to get the molar ratio of 0.22 CTAB:0.48 TEOS. It was observed that due to further increase in surfactant concentration, more surfactant cations became available for interaction with silicate anions, hence more gel formation was observed. In sample A-IV, the surfactant concentration has been increased to give molar ratio of 0.274 CTAB:0.48 TEOS. Same phenomenon was observed and more gel formation was occurred. As-synthesized samples were characterized by different techniques. Thermogravimetric analysis of as-synthesized samples was studied in the temperature range of 303 to 1173 K. Graph shows that weight loss of the sample in the three different temperature regions, first from 303 to 423 K due to the desorption of physically adsorbed water, second from 423 to 723 K due to the removal of organic template which indicate that uncalcined sample contain large amount of organic surfactant and third from 723 to 1173 k due to the water loss from the condensation of adjacent Si-OH to form Si-O-Si. These results are in accordance with the results presented by Chen *et al.* (1993), Ajaikumar and Pandurangan (2007). TGA Graph shows that at 723 K template could be removed by calcination because upto at 1093 K framework of substance remain undamaged. As-synthesized samples were characterized before and after calcination by Fourier Transform Infrared spectroscopy (FTIR). Infrared spectroscopy can be used for both qualitative and quantitative analysis of molecular species. The most widely used region is the mid-infrared that extend from about 400-4,000 cm^{-1}. The FTIR analysis shows that all the four sample have the bands at the same positions. A broad band at 3,431 cm^{-1} is a characteristic band of Si-OH and water molecules adsorbed; the bands at 2920, 2850 and 1477 cm^{-1} are characteristic bands of surfactant alkyl chain ($-CH_2$); the very weak band at 1656 cm^{-1} is associated with the bending mode of H_2O (Jiang *et al.*, 2008). The spectra in the range of 2500-400 cm^{-1} contain two main bands at ca. 1100 cm^{-1} and 800 cm^{-1} assigned to asymmetric and symmetric stretching of Si-O-Si respectively. The band at around 960 cm^{-1} is a characteristic band of mesoporous molecular sieve (MMS) that is assigned to the stretching vibration of $Si-O^-$ (Si-OH) groups. These results are also in accordance with the previous results reported by Liu *et al.* (2004).

The temperature 723 K was selected for calcination from TGA analysis. This analysis shows that organic template removed from as-synthesized samples at 723 K. Above this temperature condensation of silanol groups occurs. This temperature was suitable for calcination to observe the changes in frame work of substance. After calcinations, no spectral features were found at 960 cm^{-1} that is a peak from Si-OH, this shows a high degree of polycondensation. Thus calcination leads to the formation of Si-O-Si bonds via a polycondensation (Romero *et al.*, 1997; Grisdanurak *et al.*, 2003). The TGA analysis also confirms that weight loss of a substance from 723-1173 K is due to removal of water molecules because of condensation of adjacent silanols (Si-OH) and formation of Si-O-Si. The bands at 2,920, 2,850 and 1,477 cm^{-1} disappeared after samples were calcined at 723 k which showed that templates had been removed. However, the characteristic bands of framework still existed after calcinations which showed that the calcination at this temperature didn't significantly change the framework of as-synthesized mesoporous materials i.e., A-I, A-II, A-III and A-IV.

Surface morphology of the as-synthesized samples were characterized by FESEM. Particals in the all samples possesses spherical morphology with varied diameter range. In contrast with the spherical morphology, samples also possess irregular shape particals or agglomerates. FESEM micrographs of all samples shows that an increase in the concentration of the CTAB surfactant resulted in formation of more spherical particles are formed as shown in Fig. 4. This is because more surfactant cations were available for silicate anions for interactions and thus leading to the formation of mesoporous material increases. Overall results of FESEM showed that concentration of surfactant play very important role in the development of material.

As-synthesized samples were further studied by Elemental Dispersive X-ray. EDX analysis gives the information and confirm the elements present in the material. As synthesized materials contain silicon, oxygen, in addition to these, carbon due to surfactant residue and very little amount of aluminium were present in each sample as impurity.

CONCLUSION

The cetyltrimethylammonium bromide (CTAB) as a templating agent and Tetraethylorthosilicate (TEOS) as a silica source under hydrothermal condition were used for the formation of mesoporous material. As previously reported in several literatures, the formation of mesoporous material depends on the surfactant, without the use of surfactant amorphous product obtained. The influence of surfactant concentration on the physico-chemical characteristics of as-synthesized materials was studied. Experimental results showed that the concentration of the surfactant has influence on the formation of the material. As the concentration of surfactant increased, more silica polymerized due to the interaction between surfactant cations and silicate anions and then more mesoporous material formed. The FTIR results confirmed that the as- synthesized samples were mesoporous. The as-synthesized materials was found to be thermally stable upto 1073 K. EDX results confirmed that as-synthesized materials are composed of Silicon and Oxygen.

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