

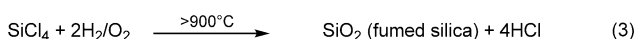
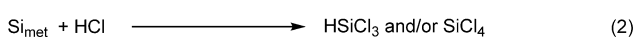
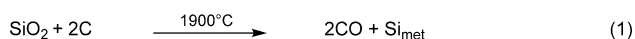
Sustainable Chemistry

Escaping the Tyranny of Carbothermal Reduction: Fumed Silica from Sustainable, Green Sources without First Having to Make SiCl₄

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Abstract: Fumed silica is produced in 1000 tons per year quantities by combusting SiCl₄ in H₂/O₂ flames. Given that both SiCl₄ and combustion byproduct HCl are corrosive, toxic and polluting, this route to fumed silica requires extensive safeguards that may be obviated if an alternate route were found. Silica, including rice hull ash (RHA) can be directly depolymerized using hindered diols to generate distillable spirocyclic alkoxy silanes or Si(OEt)₄. We report here the use of liquid-feed flame spray pyrolysis (LF-FSP) to combust the aforementioned precursors to produce fumed silica very similar to SiCl₄-derived products. The resulting powders are amorphous, necked, < 50 nm average particle sizes, with specific surface areas (SSAs) of 140–230 m²g⁻¹. The LF-FSP approach does not require the containment constraints of the SiCl₄ process and given that the RHA silica source is produced in million ton per year quantities worldwide, the reported approach represents a sustainable, green and potentially lower-cost alternative.

Fumed silica is used in multiple applications ranging from fillers to extend polymers/rubbers, as the insulating core in vacuum insulation panels, as a mild abrasive for polishing, as a thickening agent in food production, etc.^[1–5] and hence is produced in 1000 ton per year quantities throughout the world.^[6–9] Traditionally, much of the fumed silica used today comes from a sequence of reactions that actually starts with silica as illustrated in Scheme 1.



Scheme 1. Sequence of conventional procedures for fumed silica production (met = metallurgical grade, ≈ 98% purity).

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Thus, any silica source can be reacted with any carbon source in an electric arc furnace at approximately 1900 °C undergoing carbothermal reduction to metallurgical grade silicon or Si_{met} which is then treated with HCl to produce SiCl₄ which in turn is combusted in a hydrogen-oxygen flame to produce fumed silica plus byproduct HCl. The HCl is recycled with little loss. Nonetheless, because all chlorosilanes and HCl gas are corrosive, toxic and polluting, such production processes require expensive and extensive safeguards adding to the overall cost of the final products. Furthermore, because the fumed silica + HCl products must be cooled in a sealed tube that can be 100 m long, the resulting products are typically highly necked nanoparticles in chain-like manner, as seen in Figure 1, which was recently suggested to result in it exhibiting toxic behavior akin to asbestos due to strained three-membered rings, chain-like aggregation, and hydroxyl content, although this observation appears to be controversial.^[10–13]

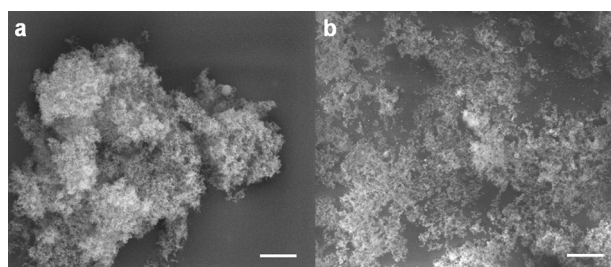
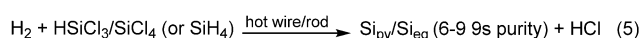


Figure 1. SEM images of fumed SiO₂. a) LF-FSP of I, b) commercial Aerosil. Scale bar, 1 μm.

SiCl₄ is a byproduct of the manufacture of solar and electronics grade silicon, [Eqs. (4) and (5) in Scheme 2]; therefore, the cost of building or running the plant to produce it is not considered in the cost of producing fumed silica. Consequently, the cost of fumed silica is artificially low.

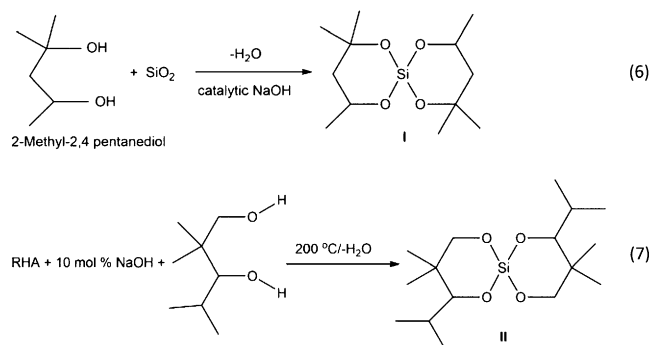
Thus, current commercial fumed silica production involves reduction of SiO₂ to the metal (e.g., Si_{met}), re-oxidation back to



Scheme 2. Sequence of procedures of solar/electronic grade silicon production.^[14]

SiCl_4 , and subsequent burning to regenerate SiO_2 . This process requires two high-temperature equipment and energy-intensive steps not to mention the safeguards needed to handle SiCl_4 and HCl . This approach is unreasonably costly and certainly illogical.

A more reasonable approach would be simply to depolymerize SiO_2 to produce volatile compounds that can be purified by distillation and/or combusted to generate fumed silica directly. However, until recently no such depolymerization chemistry was known. We recently described the first successful depolymerization of silica to produce volatile compounds, spirocyclic alkoxy silanes, that can be distilled directly from the original silica source as demonstrated by Equations (6) and (7) in Scheme 3, as well as a method of producing $\text{Si}(\text{OEt})_4$ or TEOS from related intermediates.^[15]



Scheme 3. Depolymerization of silica. Any silica source, for example, RHA can be directly depolymerized using hindered diols to generate distillable spirocyclic alkoxy silanes.

On another note, since immediate shift from SiCl_4 to alkoxy silane combustion to produce fumed silica would result in generating an enormous amount of SiCl_4 waste, it would be ideal to migrate in accordance with solar/electronic grade silicon production methods switching to metallurgical route which does not require or generate SiCl_4 during the process.^[14]

We now report the direct combustion of compound **I** and TEOS to produce fumed silica using liquid-feed flame spray pyrolysis or LF-FSP. LF-FSP, as practiced at the University of Michigan, aerosolizes metalloorganics dissolved in an alcohol fuel using O_2 .^[16–23] The aerosol is ignited using methane pilot torches and combustion occurs in a 1 m long quartz chamber *open to air*. The resulting “soot” is quenched to 300–400 °C over a distance of about 1.5 m, *rather than 100 m*, at cooling rates of approximately 1000 °C 100 ms⁻¹. The nanoparticles are then collected downstream in electrostatic precipitators operated at approximately 10 kV DC. Details on LF-FSP processing of nanopowders have been presented elsewhere.^[16–23]

The goal of the work reported here is simply to demonstrate the potential utility of direct depolymerization of SiO_2 to volatile spirocyclic alkoxy silanes or TEOS as a green and sustainable alternative to the SiCl_4 route to fumed silica.

We have not optimized the LF-FSP process and indeed recognize that it is likely not the optimal synthesis method given

that **I** and TEOS are quite volatile and their vapors should combust easily in H_2/O_2 flames without need for a solvent/fuel as used in LF-FSP. However, our extensive familiarity with LF-FSP provides the simplest test available to us for demonstration purposes. This process has potential to be competitive with the current route at commercial scales given the economic issues noted above. Below, we compare LF-FSP produced fumed silica using **I** and TEOS with Aerosil[®] fumed silica.

Figure 1 and Figure 2 provide SEM and TEM images of LF-FSP made fumed silica and Aerosil[®]. TEM images, especially, reveal aggregation for all samples, typical of flame made silicas.^[24,25]

Comparative XRDs, FTIRs, TGA and BET data presented in Figure 3, Figure 4 and Table 1 indicate that the powders are essentially identical from an analytical perspective.

Thus, the Figure 3 XRDs of as-produced fumed silica made from **I** and from SiCl_4 consist solely of a broad hump centered at 21° 2 θ , typical of amorphous materials and as expected.

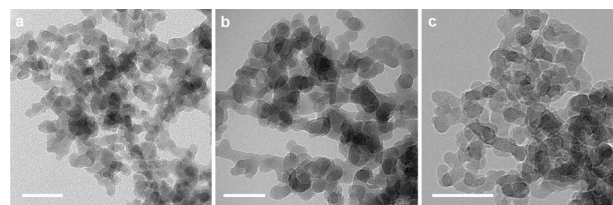


Figure 2. TEM images of fumed SiO_2 . a) LF-FSP of **I**, b) LF-FSP of TEOS, c) Aerosil. Scale bars, 50 nm.

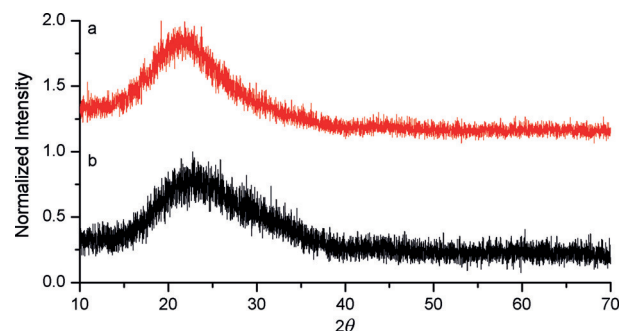


Figure 3. XRDs of fumed SiO_2 . a) LF-FSP of **I**, b) Aerosil.

Table 1. Specific surface area (SSA) of LF-FSP produced silica.			
Precursor	Solvent/Fuel	Precursor concentration [wt%]	SSA [$\text{m}^2 \text{g}^{-1}$]
I	MeOH	1	230
		3	190
	EtOH	1	220
		3	190
		5	140
PrOH	1	210	
	TEOS	1	230
3		180	
5		150	

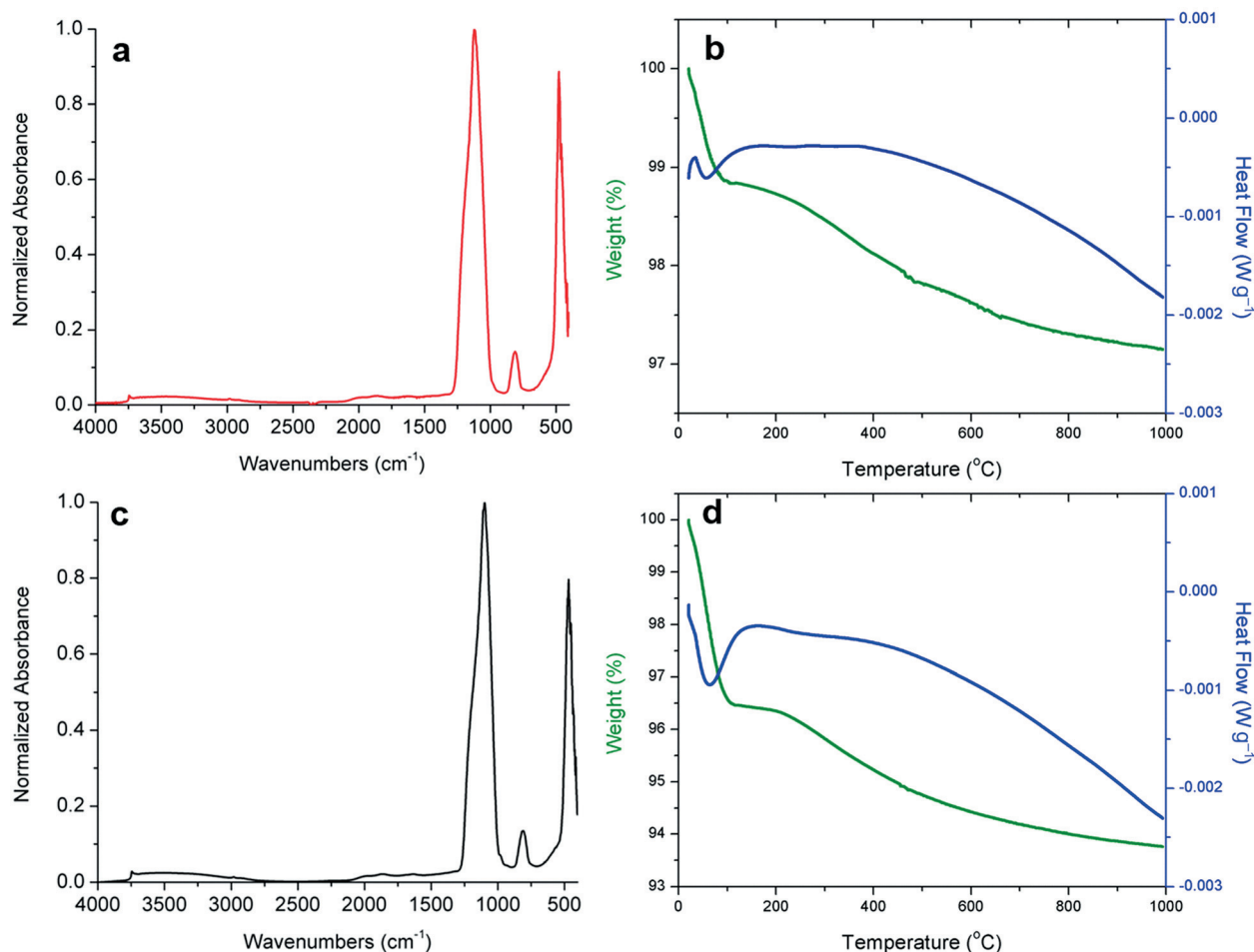


Figure 4. FTIR and TGA of fumed SiO₂. a, b) LF-FSP of I, c, d) Aerosil.

The Figure 4 FTIRs and TGAs look very similar. For TGA, the initial mass loss accompanied by a broad endotherm is ascribed to the removal of physisorbed water. The intermediate plateau at > 100 °C marks the end of physisorbed water loss. The following mass loss is from chemisorbed water, surface hydroxyl group, removal.^[26] The higher mass loss of Aerosil is merely due to higher surface area, 300 versus 190 m²g⁻¹, compared to selected LF-FSP silica.

N₂ adsorption analyses show typical SSAs of 140–230 m²g⁻¹ for fumed silica derived from I and TEOS as shown in Table 1 whereas that from SiCl₄ runs 50–400 m²g⁻¹. However, it should be noted that fumed silica from SiCl₄ is produced in a long optimized, mature process. Also, note that lower precursor concentration and lower molecular weight alcohol fuel give higher SSAs for LF-FSP while the former has a stronger effect.

These variables can be adjusted to produce silica at selected SSAs; however, the option of using H₂/O₂ flames likely offers a cleaner and lower cost mechanism to produce “green” fumed silica.

No noticeable difference is observed for fumed silica derived from I and TEOS. Hence, combustion of I would be preferred for fumed silica production since TEOS involves two synthetic steps whereas I is direct depolymerization of SiO₂.^[15]

Based on the above results, we believe that we have developed a green and sustainable route to fumed silica that offers the same if not better properties when compared with fumed silica currently produced from SiCl₄. Also, given that there are no hazardous byproducts when combusting compound I or TEOS all the safety mechanisms necessary when combusting SiCl₄, including a 100 m long tube, can be avoided, resulting in much lower overall cost, and greatly improving the space efficiency of the combustion apparatus. As a comparison, the LF-FSP apparatus is approximately 3 m long. The only true test will be to determine if it will be cost effective at scale.

A further comment is necessary. The source of the silica is rice hull ash. Rice hulls are frequently burned to produce electricity and RHA coincidentally. The actual energy generated can run to 0.6 GWh per ton.^[27] Thus, the energy required to transform RHA into fumed silica is likely to be much less than the output of electrical power on a per kg basis of fumed silica than required to produce fumed silica from SiCl₄. Furthermore, the energy gained by burning rice hulls comes from burning carbon. The rice plant has fixed this carbon by photosynthesis using CO₂ as the source. Consequently, the carbon footprint for the process demonstrated is likely near zero. Likewise the energy output will be more than the energy required to produce the fumed silica.

Experimental Section

Materials

Spirocyclic alkoxy silanes **I** and TEOS were synthesized using methods described in our recent paper.^[15] Methanol, ethanol, and propanol were purchased from Decon Labs (King of Prussia, PA). Aerosil 300 was purchased from Evonik.

LF-FSP

Methanol, ethanol or propanol solutions of **I** and TEOS were obtained by dissolving sufficient **I** and TEOS to make a 1, 3 or 5 wt% silica ceramic yield solution. **II** was not tested due to similarity with **I**, to avoid redundancy. The general methods for conducting LF-FSP have been described in previous papers.^[16–23]

Analytical techniques

Thermal stabilities of materials under synthetic air were measured on a Q600 simultaneous TGA-DSC instrument (TA Instruments, Inc., New Castle, DE). Samples (15–25 mg) were placed into alumina pans and then ramped from 25 to 1000 °C (10 °C min⁻¹). The air-flow rate was 60 mL min⁻¹.

XRD analyses were run using a Rigaku rotating anode goniometer (Rigaku Denki, Ltd., Tokyo, Japan). XRD scans were made from 10° to 70° 2θ, using a scan rate of 2° min⁻¹ in 0.01° increments and Cu_{Kα} radiation (1.541 Å) operating at 40 kV and 100 mA.

SEM micrographs were taken using a FEI NOVA Nanolab system (FEI company, Hillsboro, OR). The powders were sputter coated with gold/palladium using a Technics Hummer IV DC sputtering system (Anatech, Ltd., Alexandria, VA).

High resolution TEM (JEOL 3011, Osaka, Japan) was used to measure the particle sizes and morphologies of as-produced powders. Samples were prepared by dipping a holey carbon grid in a vial of dispersion with fumed silica powder. The specimen was held in a Gatan double tilt goniometer. An operating voltage of 300 kV was used.

Specific surface areas were obtained using a Micromeritics ASAP 2020 sorption analyzer. Samples (400 mg) were degassed at 400 °C/5 h. Each analysis was run at -196 °C (77 K) with N₂. The SSAs were determined by the BET multipoint method using ten data points at relative pressures of 0.05–0.30.

Acknowledgements

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Keywords: flame spray pyrolysis · fumed silica · green chemistry · rice hull ash · spirocyclic alkoxy silanes

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