Article

Preparation and Characterization of Mesoporous Silica from Bagasse Bottom Ash from the Sugar Industry

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Abstract: A novel and sustainable process to recycle an environmentally injurious material rich in silica—waste bagasse bottom ash from the sugar industry—into mesoporous pure silica of high purity is reported. Bagasse bottom ash (BBA) is a major by-product of the sugar industry, with very inadequate recycling possibilities due to environmentally detrimental pollutants, whose production is dramatically increasing. In this study, for the first time, more than 90% of the silica from the bottom ash could be extracted for the synthesis of mesoporous silica using a low-temperature alkaline dissolution method instead of the customary elevated-temperature process. Furthermore, the process of dissolution was thoroughly studied to obtain the essential insight into silica hydrolysis that is largely missing from the existing research literature. Under alkaline conditions, the hydrolysis of silica is hindered due to the formation of zeolite and protective layers around the etching particles. This layer becomes a protective barrier that hinders the mass transfer of silica monomers to the solution, thus halting the dissolution process. Therefore, sequential extractions with optimized conditions of 100 °C for 72 h were employed to attain maximum silica extraction efficiency.

Keywords: bagasse bottom ash; green synthesis; water glass; mesoporous silica

1. Introduction

Sodium silicate, which is also known as water glass, is an important raw material, and finds applications in paints, paper, detergents, zeolites, and the building materials industry [1–3]. In terms of volume, water glass is the most widely used synthetic chemical after bases and acids [4]. However, the existing commercial manufacture protocol requires a huge input of energy. Moreover, it contributes a huge quantity of CO_2 to the environment. One main manufacture protocol is the fusion of high-grade quartz with Na_3CO_3 between 1300 and 1550 °C [5]. Due to high energy consumption and use of the reagents, the estimated amount of CO_2 that is produced for every kg of water glass is more than 1.5 kg [6]. Therefore, it is essential to find environmentally friendly methods of producing water glass with a low carbon footprintwater glass. Dissolution of silica-rich waste materials at low temperatures could provide such an alternative sustainable method for the synthesis of this widely consumed raw material. In addition to the lower energy demand and minimal CO_2 footprint, these methods can also reuse waste materials that would otherwise be landfilled, and possibly be harmful to the environment [7,8]. Silica-rich ashes from different sources—such as coal combustion, rice husk, and waste incineration—have been investigated for the recovery of silica [9–11]. The most commonly used method for the dissolution of silica from these residues to produce water glass is by fusion, in which the ashes are fused with a sodium carbonate at high temperatures (700–1000 °C) and subsequently dissolved. Moreover, BA from coal combustion is more frequently investigated for the preparation of specialty silica [12]. However, despite the presence of

silica in an amorphous form, less than one-third of the total available silica could be recycled. This incomplete dissolution and use of high temperatures hinder the wide-scale application of these processes. Bottom ash obtained from the burning of municipal waste is also a rich waste material. BBA is waste produced by the sugar industry, containing both silica and a number of other ingredients in different proportions. This ash creates a lot of environmental issues rather than a useful utilization. Thus, the recycling of this ash into a useful product has been a challenging task for chemists working on environmental issues. The recycling of bagasse ash has been reported by the author in different ways, including cement raw materials [13], cement replacement from mortar [14], geopolymerization [15], etc. Other ashes have also been recycled in different ways, such as silica extraction from municipal solid waste by coalescing it with lithium metaborate at 900 °C in a muffle furnace [16]. In the aforementioned study, most of the consideration was given to the extraction of silica rather than the mechanisms and parameters affecting the silica dissolution. The basic knowledge regarding the extraction of silica, in addition to associated modifications in its mineralogical composition, is still under investigation. Regardless of the initial silica source used for extraction, high-temperature fusion processes produce a low yield of silica (≈33%) [17,18]. Moreover, it would be more important from both the commercial and environmental perspectives for silica dissolution to be attainable at lower temperatures by using bagasse bottom ash from the sugar industry.

Mesoporous silica has a number of diverse applications including immobilization of β-glycosidase by templating with tannic acid [19]; β-glucosidase was immobilized by adsorption on synthesized tannic acid-templated mesoporous silica nanoparticles. The synthesis procedure adopts a green, cheap, and biocompatible templating agent. Textural and morphological characterization was performed. Mesoporous silica has also been used for the adsorption of cellulose [20]. Mesoporous silica materials—due to their tunable pore size, large surface area, and easy functionalization—offer a unique opportunity for enzyme immobilization. However, a significant enhancement of the activity of cellulase enzymes entrapped within the silica pores still represents a challenge. Mesoporous silica nanoparticles with a large surface area and pore volume have attracted considerable attention for their applications in drug delivery and biomedicine [21].

In the present work, the synthesis of water glass at a low temperature, using bagasse ash as a source of silica, and its consequent utilization for the preparation of mesoporous silica, is presented for the first time. During the process of extraction, mineralogical alterations in BBA residue were studied to ascertain the mechanism for the extraction of silica from the BBA. Moreover, the overall mechanism of dissolution of silica from BBA, along with the production of water glass and high-purity structured mesoporous silica from a low-cost raw material using a green and sustainable production method, is presented.

2. Materials and Methods

2.1. Bagasse Bottom Ash

The Bagasse bottom ash was obtained from the premier sugar mill at Mardan, Khyber Pakhtunkhwa, Pakistan. In order to obtain particles below 125 μm in size, milling was performed by a laboratory milling process.

2.2. Chemical and Mineralogical Analyses

Chemical composition of BBA was studied using X-ray fluorescence (Panalytical Epsilon); for this purpose, BBA was mixed with flux ($Li_2B_4O_7$ and $LiBO_4$) and lithium bromide (LiBr) as a wetting agent. The mix was fused in an oven (LabTech) at 1100 °C. Prior to fusion, loss on ignition was measured; for this purpose, 2 g of dried residue was placed in a crucible, which was then heated to 600 °C for 7 h to obtain constant mass. Mineralogical analysis of the original BBA and residue left from the silica extraction was performed. Mineralogical study was carried out using XRD (Bruker) with Kα1 and Kα2 of 1.7901 and 1.7929 Å, respectively. Samples were powdered to a grain size of ≤ 10 μm,

and then 10 wt% Si was mixed with the sample as an internal standard to measure the amorphous content.

2.3. Silica Extraction

The pretreatment of BBA was performed with 4 M HNO$_3$; for this purpose, nitric acid was mixed with bagasse ash, and the mixture was stirred for one day and night (24 h) at 25 °C. Silica precipitation was completed by allowing the mixture to settle for two days (48 h). The treated ash was separated using filtration and used for the extraction of silica. Dissolution of silicates was studied at different reaction times of 24, 48, and 72 h, and temperatures of 20, 40, 60, 80, and 100 °C, keeping the liquid-to-solid ratio as 1:2, to find out the optimal settings for the dissolution of silica in the presence of NaOH. Preliminary experiments were performed with an L/S ratio of 1:2 in order to understand the effects of reaction interval and temperature on silica dissolution without reaching saturation. Once optimal conditions were determined, the extraction of silica was carried out by mixing BBA with NaOH solution at a ratio of 1:25 (wt:vol). The residues from extraction were dried and examined using X-ray fluorescence in order to study the silica that remained from the extraction process. The difference between total silica in BBA and that of soluble silica was used to calculate the extraction efficiency. The efficiency of silica extraction was calculated as follows:

$$EE\ (\%) = SiO_{2\ residue} / (SiO_{2\ total} - SiO_{2\ quartz}) \times 100 \tag{1}$$

2.4. Preparation of Mesoporous Silica

First, 1.194 g (3.28 mmol) of cetyltrimethyl ammonium bromide (C$_{19}$H$_{42}$BrN) was added to 114.1 g of the extracted silicate solution from the first of three 48-h, 70 °C extractions. The mixture was kept at 70 °C for two hours, and then the pH was slowly decreased to 9, using 2 M HCl. The precipitate obtained before filtration was kept in a sealed vessel for three days (72 h) at room temperature and then filtered off, washed thoroughly using double-distilled water, dried, charred, and then heated at 1000 °C using a muffle furnace for 30 min. The resulting mesoporous silica was studied for phase identification using X-ray diffraction.

3. Results and Discussion

3.1. Characterization of BBA

The elemental composition of BBA, as obtained from XRF, is given in Table 1. It is clear from the table that SiO$_2$ is the highest component of the ash (58.8 wt%), along with other major oxides. The mineralogical composition of the original BBA as obtained from XRD studies is provided in Figure 1a. From the figure, it is clear that BBA mainly contains quartz, calcite, iron oxide, calcium oxide, and cristobalite.

Table 1. Chemical composition of bagasse bottom ash (BBA), acid-treated bagasse bottom ash (TBBA), and obtained silica in wt%.

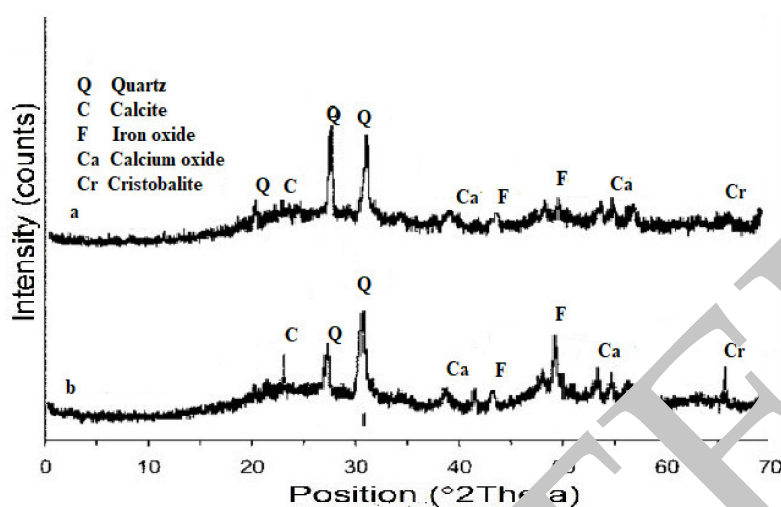|	SiO$_2$	CaO	Al$_2$O$_3$	Fe$_2$O$_3$	Na$_2$O	MgO	K$_2$O	ZnO	CuO	LOI
BBA	56.52	14.62	7.93	6.44	2.92	2.01	0.91	0.34	0.32	2.75
TBBA		9.87	7.63	3.56	2.51	1.54	0.82	0.22	0.12	16.33
Mesoporous Silica	99.32	0.22	0.30	0.04						

Figure 1. XRD pattern of original bagasse bottom ash (**a**) and acid-treated ash (**b**).

3.2. Pretreatment of BBA

Acid treatment of BBA was performed in order to remove contaminants. The XRD peaks of acid-treated BBA are represented in Figure 1b. During the treatment, the carbonate minerals such as dolomite and calcite decomposed, as confirmed by the figure. It has been reported in earlier studies on BBA that carbonate minerals act as a pool of metal ions—particularly Zn and Cu [8]. Therefore, as a result of the treatment, these ions are reduced in the ash, as clear from Table 1. Moreover, iron oxide is almost entirely dissolved, with partial dissolution of the cristobalite phase. No effect is observed on the quartz, showing that it cannot be dissolved with the addition of acid. The silicate dissolved was transformed into gel-like silica due to polymerization at low pH, which can be removed alongside the residual acid through filtration. Resultantly, a minor decrease in the amount of silica (2 wt%) was observed during the acid treatment of BBA, and the acid-treated bagasse bottom ash (TBBA) was found to contain 66.9 wt% of SiO_2 (Table 1).

3.3. Silica Extraction

Preliminary silica extraction from BBA was carried out to observe the dissolution behavior of silica and the establishment of subordinate silicate classes. The influence of temperature and reaction duration was studied to discover the optimal conditions to obtain the highest extraction of silica. The extraction efficiency under changing reaction conditions is shown in Figure 2. It can be seen in the figure that dissolution of almost 20% of silica takes place at 20 °C during the first 24 h, which increased almost twofold as the reaction time was doubled. Furthermore, as the reaction time was increased to 72 h while maintaining the same temperature, a very minute increase in EE was observed (~40–45%). Cristobalite (silicate mineral) in ash is considered to be the initial source of this silica, a small quantity of which was perceived in the as-received BBA (Figure 1a). Acid treatment causes the conversion of silicate to silica, which precipitates and is preserved for the resulting dissolution in basic medium. The intensification of silica in solution at reaction times longer than 24 h shows the continuous dissolution of soda lime glass that is present in BBA. Moreover, even at the longest reaction times of 72 h at the same temperature—i.e., 20 °C—only an EE of 45% can be achieved. When the medium is made alkaline with a pH greater than 13, silica dissolution begins, in which the silica framework is damaged, thereby liberating soluble silica in solution as per Equations (2) and (3).

$$-[Si–O–Si] - +OH \rightarrow -[Si–OH] + -[Si–O] \tag{2}$$

$$-[Si–O] + H2O \rightarrow -[Si–OH] + OH \tag{3}$$
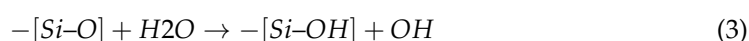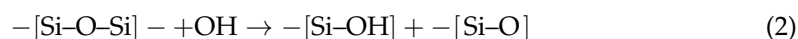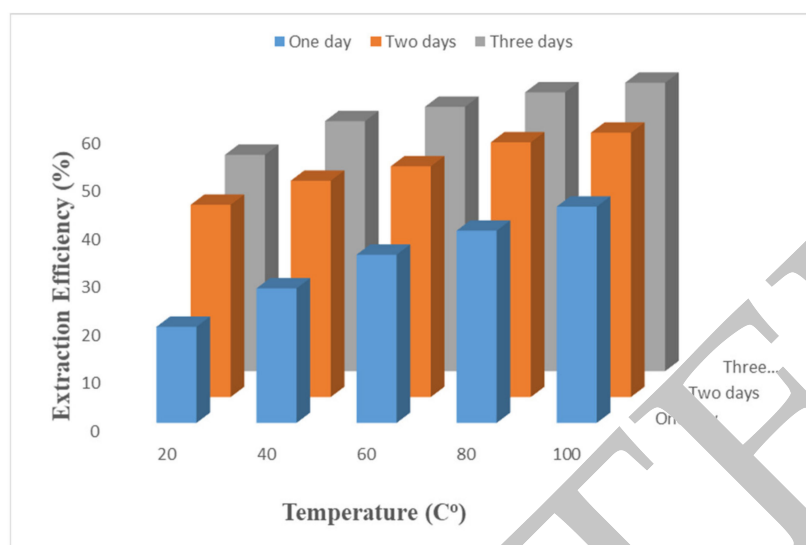
Figure 2. Effects of temperature and reaction time on the extraction efficiency of silica (SiO_2) from bagasse bottom ash.

It has been reported in previous research [22,23] that, in order to improve the glass dissolution at higher pH, the use of non-ambient temperature is required. For this purpose, the process was carried out at temperatures as high as 80 and 100 °C for the dissolution of maximum ash. It can be seen from Figure 2 that the amount of dissolved silica increases with the increase in reaction temperature. Performing the extraction reaction at 80 °C for 48 h, 50% of silica was in the solution. Moreover, no substantial change in extraction efficiency was observed upon further increase in temperature to 100 °C. Therefore, the optimal reaction time was found to be 48 h, with an optimal temperature of 80 °C, for maximum dissolution of ash. However, under such circumstances, about half of soluble silica may be extracted, showing that controlling parameters hamper the dissolution's progression.

In basic medium, dissolution of glass depends on the transformation of soluble silica from impression particles of glass [24]. Under such circumstances, glass is continuously dissolved until the secondary silicate species begins precipitation and a layer deposits on the surface of the glass. As a result of this thin layer's formation, transfer of mass is slowed down, consequently slowing the development of inclusive dissolution [25]. It was also observed that the reaction temperature and amorphous silica dissolution are directly related to one another. Similarly, when the silica extraction experiment was carried out at 100 °C, the amorphous portion of the ash was considerably reduced. On the other hand, it is important to mention that the histrionic intensification of dissolution at 100 °C does not increase the amount of soluble silica in the solution. Under such circumstances, an extraction efficiency of 50% is observed, which is the same as at 80 °C (Figure 2). XRD of residue achieved at a temperature of 100 °C (Figure 3c) shows the formation of a zeolite phase as a byproduct. The existence of zeolite in the residues shows that the solution after extraction was saturated in terms of silica with a significant amount of reactive Al^{3+} ions for the formation of zeolite. It was observed that the glass solubility increases histrionically as the formation of the zeolite phase develops, which is in close agreement with the findings of Fournier et al. The development of zeolite utilizes the soluble silica and increases the equilibrium as a result of the dissolution of glass. As a result, to compensate for the soluble silica, further dissolution of glass occurs, which is used during the secondary silicates' precipitation. Hence, this unwanted development of zeolite reduces the amount of silica in solution, using it in the development of zeolite. Moreover, some amount of calcite is also observed in the residues remaining from the desilication process. The appearance of calcium oxide is a result of the dissolution of calcite, which leads to the absorption of carbon dioxide from the atmosphere, resulting in the formation of carbonate species.
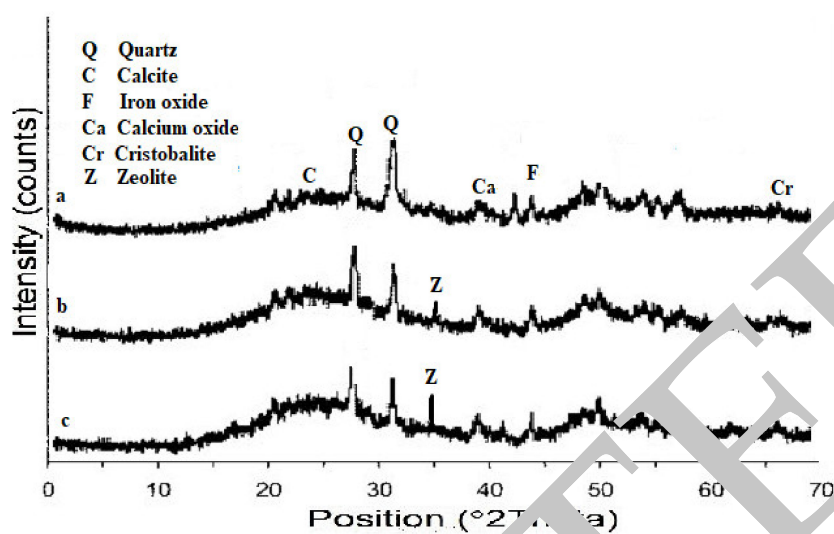
Figure 3. XRD pattern of ash residues recovered after extraction for two days at 20 °C (**a**), 40 °C (**b**), and 100 °C (**c**).

Successive silica extraction was carried out to achieve greater silica extraction efficiency from BBA, while avoiding the precipitation of secondary silicate species. Therefore, extraction was carried out with optimal conditions, i.e., 100 °C and 3 days.
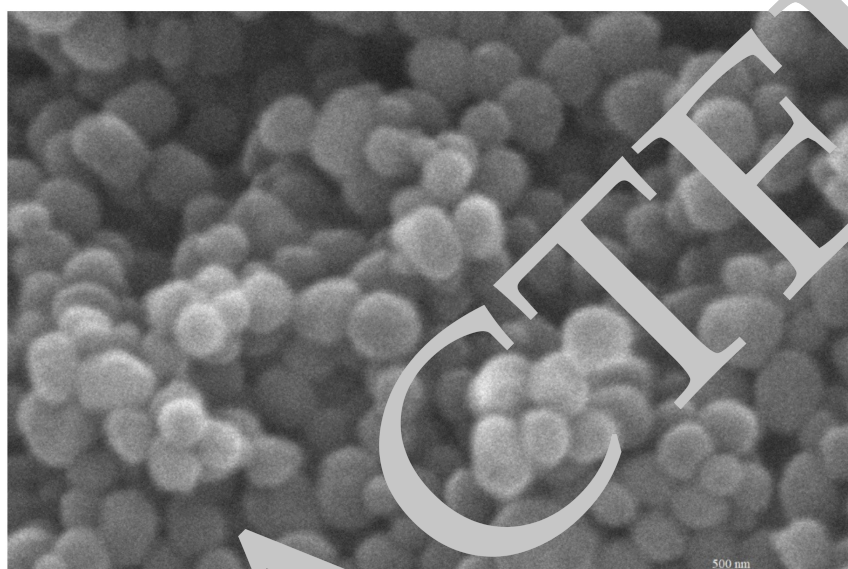
3.4. Mesoporous Silica

Figure 4 shows the XRD pattern of mesoporous silica obtained as the final product. The pattern confirms the presence of ordered mesostructured silica with an amorphous nature. The amount of mesoporous silica was calculated from the mass difference between the starting BBA and the final residue, and was found to be 20 mmol of silica. The molar ratio of cetyl-trimethyl-ammonium bromide to silicate was chosen to be 0.16:1, which has been shown to be the optimal ratio by Yan et al., who studied the synthesis of mesoporous silica using cetyl-trimethyl-ammonium bromide and a sodium silicate solution extracted from coal combustion fly ash [26]. This low-surfactant-concentration method was chosen to minimize problems that arise from high surfactant concentrations, such as high viscosity and the high surfactant requirements.
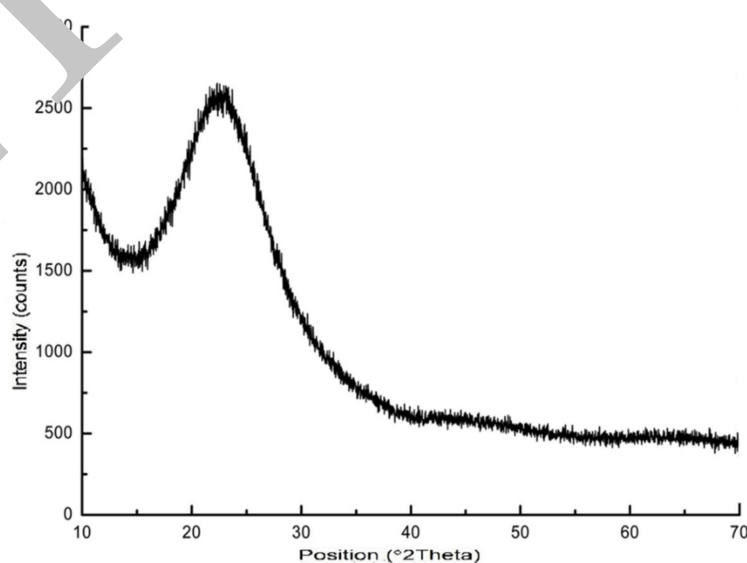
Figure 4. XRD pattern of the mesoporous silica synthesized from bagasse bottom ash.

An SEM image of the synthesized mesoporous silica is given in Figure 5. The structure is slightly disordered, which may be due to positive iron ions in the solution during its formation [27], while the final product is 99.32 wt% pure silica, as shown in Table 1. The silicate solution used may still contain iron and other cations. Anions of silicate attract the respective cations, which may be amalgamated during condensation into the structure. Some defects in structure may also be created, producing a long-ranged structure with the same flaws, a mesoporous structure with a large specific surface, and good pureness.

Figure 5. SEM image of mesoporous silica obtained from Bagasse bottom ash.

4. Conclusions

This study provided an environmental friendly, low-cost, and sustainable process for the preparation of sodium silicate and high-purity mesoporous silica. This study also introduced an economical and green synthetic route at low temperature for the synthesis of sodium silicate from bagasse bottom ash with a high silica extraction efficiency. A thorough characterization showed that BBA contains more than 58 wt% of silica in both crystalline and amorphous forms. Additionally, these residues contain different contaminants, such as heavy metals, due to which their applications are limited. Therefore, an initial acid treatment was devised that reduced these undesired constituents, increased the amorphous silica content, and made the already-present silica more soluble by increasing its surface area. Analysis of acid-treated BBA showed elimination of carbonates and an increase in amorphous silica; thus, this material is considered to be the ideal source of silica for sustainable extraction. Extraction experiments showed a clear correlation between the extracted silica and the process conditions, such as the reaction time, temperature, and liquid-to-solid ratio. Low extraction efficiencies of silica were observed under conditions with low temperatures and short times due to incomplete dissolution of the soluble silica. On the other hand, at a relatively high temperature of 100 °C, with a long reaction time and low liquid content, the critical saturation point was reached, causing the formation of insoluble zeolites and, thus, reducing the amount of soluble silica. The optimal conditions for silica extraction were found to be 100 °C and 72 h. By using a sequential extraction, more than 80 wt% of the available silica can be recovered from the BBA residues. In order to demonstrate its application potential, mesoporous silica was obtained from BBA that was extracted from sodium silicate solution. The obtained mesoporous silica had a high surface area (870 m^2/g) with high purity (98.5 wt%). Thus, a novel and sustainable application of BBA and a sustainable synthesis route for the production of high-quality silica products are reported.

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