Recent Progress on the Development of Engineered Silica Particles Derived from Rice Husk

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Abstract: The development of engineered silica particles by using low-cost renewable or waste resources is a key example of sustainability. Rice husks have emerged as a renewable resource for the production of engineered silica particles as well as bioenergy. This review presents a state-of-the-art process for the development of engineered silica particles from rice husks via a bottom-up process. The first part of this review focuses on the extraction of Si from rice husks through combustion and chemical reactions. The second part details the technologies for synthesizing engineered silica particles using silicate obtained from rice husks. These include technologies for the precipitation of silica particles, the control of morphological properties, and the synthesis of ordered porous silica particles. Finally, several issues that need to be resolved before this process can be commercialized are addressed for future research.

Keywords: rice husk; rice husk ash; silica; engineered particle; bottom-up process; silica extraction; valorization; agricultural byproduct; sustainable material; biomass; renewable material

1. Introduction

Global rice and paddy production in 2018 was approximately 996 million tons as reported by the Food and Agricultural Organization [1]. The countries with the largest volume of rice and paddy production are located in Asia (China, India, Indonesia, Bangladesh, Vietnam, and Thailand). Rice husk is a residue produced during the rice mill process and on average, accounts for 20% of the paddy produced. The rice husk output in 2018 was approximately 199 million tons. Many countries use rice husks as a renewable energy resource for power generation [2]. The heating value of the rice husk is 15 MJ kg⁻¹, and there is an energy potential of 2985 PJ available per year [3]. Currently, rice husks are burnt in simple incinerators for resident energy, industrial streams, and thermal power plants in most Asian countries. Several Asian countries such as India, China, and Thailand are operating gasification power plants using rice husks [4,5]. Gasification power plants using rice husks have power capacities ranging between 20 and 400 kWe; however, they are still in the demonstration stage [6]. One ton of rice husk generates 800 kWh of electric power [7] and after generating electric power, approximately 0.195 tons of rice husk ash is produced as a byproduct. High ash content in rice husks causes operational problems and consequently renders their thermal conversion difficult and expensive. Therefore, the valorization of rice husk ash for value-added material applications is important for improving the economic return of the entire process. In addition, the extraction of inorganic compounds from rice husks before energy generation could be worthwhile to reduce the burden of the energy production process.
Rice husk ash mainly contains amorphous silica ($\text{SiO}_2$) and other metallic impurities. Rice husk-derived silica has gained increasing interest as a renewable source. Engineered silica particles have recently been intensively studied for bio-applications [8–10], energy storage [11,12], bioremediation [13], and as construction materials [14–17]. By increasing the utilization of engineered silica particles, the synthesis of engineered silica from renewable resources is considered to enhance sustainability. The use of rice husk silica for synthesizing engineered silica particles has advantages not only in the economy but also in mitigating environmental issues [18].

However, there is lack of comprehensive articles on the recovery and synthesis of silica particles derived from rice husks. Therefore, this review presents the recent progress in the development of engineered silica particles derived from rice husks.

2. Purified Silica Extraction from Rice Husk

2.1. Combustion to Remove Organic Contents

The most widely used method for obtaining silica from rice husks is direct combustion, resulting in the production of rice husk ash, which contains 85–95% silica [19–21]. The direct combustion of rice husk can produce thermal energy and can be used to generate steam, which subsequently drives the blades of a turbine to produce electricity. However, the direct combustion of rice husks generates greenhouse gases and emits significant quantities of particulate matter [22,23]. The emissions from rice husk burning contain CO$_2$, CH$_4$, CO, NO$_x$, SO$_2$, PM$_{2.5}$, and PM$_{10}$ of black carbon. Hence, when using direct combustion, it is important to always use both a dust collector and a gas absorber. The emission of CO$_2$ from rice husk combustion is “net zero” because the hull reduces CO$_2$ in nature. It also replaces the use of a fossil fuel. Therefore, the use of rice husk to produce energy is encouraged only when it is installed with emission control devices.

The phase change of silica depends on the combustion temperature. The silica in rice husks is a non-crystalline phase. As the combustion temperature increases over 600 °C, the phase transformation to tridymite and cristobalite starts [24]. However, the crystallization temperature varied depending on the chemical composition of rice husk ash [25]. It was also reported that pretreated rice husk remained amorphous up to 1000 °C. At higher combusting temperatures, the physical properties of silica also change. Zareihassangheshlaghi et al. compared the physical properties of rice husk ashes synthesized at 700 and 900 °C [26]. At a higher combustion temperature (900 °C), fewer metal impurities were observed. This might be due to the formation of more volatile and less stable phases that can be easily released into the gas phase. At this temperature, alkaline earth metal oxides can be refractory. At higher temperatures, the size of ash particles increases. Furthermore, the mesopores and micropores in the ash diminish after combustion at 900 °C. In rice husk ash, alkali metal impurities, such as K, P, Ca, and Mg, incorporate and form sticky alkali silicate at high combustion temperatures. This causes ash melting and agglomeration, which increases the size of particles and diminishes the meso- and micro-pores [27].

Previous studies report that combustion conditions could define the characteristics of silica; however, changes in characteristics could be within a narrow range: the specific surface area (11–39 m$^2$ g$^{-1}$), purity (29.7–96.7 wt %), and crystallinity (completely amorphous or partially crystalline) [25]. The characteristics of the shape, particle size, pore, and uniformity cannot be controlled by changing the combustion conditions. Therefore, chemical treatment should be followed to synthesize the engineered silica particles.

2.2. Principle of Chemically Extracting Silica from Rice Husk

The main components of rice husk—cellulose, hemicellulose, lignin and inorganics—can be separated by their thermo-chemical properties. Figure 1 shows the phase changes of rice husk components depending on pH. Under acidic conditions, cellulose and hemicellulose are dissolved in the aqueous phase and can be separated from solid residues, mainly lignin and inorganics [28].
During the hydrolysis of polysaccharides, metallic impurities, such as K₂O, P₂O₅, CaO, and MgO, were discarded by the washing step. Alkaline hydrothermal conditions induce the cleavage of ester linkages in lignin, which dissolves the lignin. After alkaline hydrothermal treatment, lignin can be removed from the solid residue [29,30]. The alkaline thermal treatment also dissolves silica and partially dissolves xylan to the liquid phase. The solubility of amorphous silica rapidly increases above pH 9.14 [31]. It can be again solidified by decreasing the pH. During solidification, silica particles can be engineered to have specific properties fit for their intended purpose. Residual organic compounds in the silica can be thermally removed at temperatures over 575 °C.

![Figure 1. Phase change of rice husk components depending on pH.](image)

### 2.3. Acid Leaching to Obtain High Purity Silica

Acid leaching to remove organic matter and metallic impurities from rice husks was conducted before or after the combustion process. Acid leaching can produce a higher purity and specific surface area when compared to without acid leaching [19,32–34]. Lee et al. compared the performances of three acid solutions—sulfuric acid, hydrogen chloride, and oxalic acid—to remove the organic matter and metallic impurities [19]. Sulfuric acid effectively dissolved and removed both cellulose and hemicellulose but was not effective in removing lignin. Both hydrogen chloride and oxalic acid mainly reduced hemicellulose. The removal of metallic impurities was investigated depending on the acid solutions. However, the capability of acid solutions to remove organic and metallic impurities in rice husk varied depending on the solution’s concentration, and the reaction time and temperature [35]. Traditionally, the acid leaching of rice husk was performed with sulfuric acid, hydrogen chloride [36], and nitric acid [33]. The use of a strong acid solution is significantly hazardous to the environment and human life. In addition, strong acid leaching produces not only soluble sugars but also smaller compounds such as aliphatic carboxylic acids and furans, which are inhibitors to microbes and enzymes. Therefore, attempts to replace these strong acid agents with environmentally harmless agents have been reported [19,37–40].

The environmentally harmless agents used to remove organic matter in rice husks were citric acid, ionic liquid, and deionized water. The use of citric acid could remove metallic impurities such as Na, K, Ca, Mg, Fe, Cu, etc., through a chelate reaction between carboxyl groups and metal elements [37,38]. Ionic liquids are green solvents and are effective in dissolving polysaccharides. The ionic liquids used to remove polysaccharides and metallic impurities from rice husks were 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium hydrogen sulfate. The dissolved cellulose can be recovered...
by mixing with distilled water and further used to produce fermentable sugar [41]. Trinh et al. reported that ionic liquid-treated cellulose significantly changed its crystallinity, surface morphology, and composition, resulting in improved enzymatic digestibility. Conventionally, lignocellulose in rice husks is simply burned to generate energy, which leads to air pollution. However, the use of ionic liquid-treated cellulose to produce biofuel does not produce any pollutants. Therefore, using ionic liquids improves both the purity of silica and the comprehensive utilization of lignocellulose. Shen et al. used deionized water to leach metallic impurities, but water leaching was effective only on the external surface [40]. Mochidzuki et al. performed water leaching under pressurized conditions using a batch autoclave and steam explosion [42]. Both autoclave hot-water and steam-explosion-treated silica showed improved purities, even comparable to those obtained with the hydrochloric acid treatment. The pressurized water treatment dissolved some portion of the silica in hot water and changed its structure, which is more applicable to the synthesis of water-glass-like materials.

Most studies reported that acid leaching could improve the amorphousness of silica [19,39,43]. Alkali metals in rice husks facilitate the initiation of the formation of cristobalite, which causes the phase transformation of the silica [44]. Acid leaching could remove alkaline metals, which prevent the phase transformation of the silica. In addition, Real et al. reported that the leaching of rice husks with an acid solution before their combustion would yield silica powder with a high specific surface area [32]. However, if the acid leaching was performed after combustion, the specific surface area of silica would be poor.

2.4. Alkali Extraction to Obtain Silicate

Silica can be extracted from rice husk by solubilizing it in an alkali solution and precipitating in an acidic medium. In general, sodium hydroxide was used to extract silica from the rice husk as sodium silicate. The following formula represents the chemical reaction:

\[
\text{SiO}_2 (s) + 2\text{NaOH} (l) \rightarrow \text{Na}_2\text{SiO}_3 (l) + \text{H}_2\text{O} (l)
\]  

Various hydrothermal conditions were used for the alkali extraction of silica. Most studies have prepared rice husk ash or acid-treated rice husk before the alkali extraction. Typically, thermal treatment is performed before alkali extraction to remove lignin. Otherwise, both lignin and silica were extracted from rice husks by alkali solution, which affected the quality of sodium silicate. In addition to the thermal treatment, organosolv fractionation can be applied to separate lignin by organic solvents such as ethanol [45] and 1,4-butanediol [46]. Rice husk ash was dissolved in sodium hydroxide solution at 80 °C [47], 90 °C [21,48], 100 °C [49], and even 150 °C [50]. In addition, a considerable amount of research has reported the performance of alkali extraction at room temperature [51–55]. In this case, rice husk ash was ground down to micron-sized particles and reacted for 24 h. The concentrations of sodium hydroxide were varied in the range of 1–10 M, which determined the reaction time. Bazargan et al. showed the removal of lignin and silica from the rice husk, not rice husk ash, by the assistance of sodium hydroxide and hydrogen peroxide [56]. However, recoveries of silica and lignin in alkaline peroxide solution were only 75 and 60%, respectively. Alkali extraction degrades lignin into phenolic compounds, such as benzoic acid, ferulic acid, and coniferyl aldehyde, and those cannot be utilized in further process.

3. Synthesis of Engineered Silica Particles Using Silicate Extracted from Rice Husks

As mentioned before, there is a limitation in changing the structure and shape of silica by changing the combustion conditions. Therefore, we focused on various methods for the synthesis of engineered silica particles using a sodium silicate solution extracted from rice husks. Such methods are based on a bottom-up process in which nano- or micron-sized particles are formed through chemical reactions of precursors at the atomic or molecular level. Although the overall synthetic procedure is relatively complex compared to methods based on a top-down process, the bottom-up process enables the precise
and uniform control of the morphological properties of products. Accordingly, in modern industries that require biomass-derived silica, it is expected that research on the development of advanced synthetic techniques based on bottom-up processes will be more actively conducted in the future.

3.1. Simple Precipitation of Silica Particles by the Addition of Acidic Reagents

To obtain silica particles from a silicate solution, the pH of the solution should be adjusted to certain ranges to induce the precipitation of silica. Because the solubility of silica increases as the pH of the solution increases, the use of acidic reagents is the basic requirement for lowering the pH of an alkaline silicate solution [57]. The precipitation reaction of silica is simply described by the following equation, where H$_a$X is an acidic molecule:

$$\text{Na}_2\text{SiO}_3 + n\text{H}_a\text{X} \rightarrow \text{SiO}_2 + n\text{Na}_a\text{X} + \text{H}_2\text{O} \quad (2)$$

Neutralization of sodium silicate solution using sulfuric acid is a common method for the precipitation of silica particles [58–63]. For example, in the paper reported by Ghorbani et al. [60], sodium silicate solution prepared from rice husk was titrated with diluted sulfuric acid to pH 7 under vigorous stirring. The solution was further stirred for 24 h and then aged for 48 h at room temperature. After filtration and washing, the obtained silica gel was freeze-dried overnight. Amorphous silica particles prepared by this process exhibited an aggregated form of primary particles with an average size of ~200 nm, and the products showed a relatively high surface area of 409 m$^2$ g$^{-1}$. The agglomerated forms of silica particles were identically observed in other studies, where the silicate solution was titrated using sulfuric acid, although the sizes of the primary particles were different in each case [61–63].

The optimized process for the synthesis of pure silica nanoparticles reported by Nassar et al. was as follows [62]: (i) Dried rice husk was acid-leached by 2 M nitric acid solution; (ii) After washing and drying, the dried residue was calcined at 600 °C; (iii) The obtained rice husk ash was refluxed with 2 M NaOH solution; (iv) The sodium silicate solution was separated by filtration; (v) The silicate solution was titrated with 1 M sulfuric acid until the pH reached 7; (vi) The obtained silica gel was aged for 24 h, and then calcined at 800 °C. The final product prepared by this process exhibited peanut-like or irregularly shaped particles (Figure 2a,b). The TEM image shows irregular shaped particles composed of tiny nanoparticles that are 10–50 nm in size.Adam et al. reported the sol–gel synthesis of silica nanoparticles from rice husk using a template-free approach [64]. They simply titrated sodium silicate, which was obtained from rice husk, with nitric acid until the pH reached 9.0. After aging for 2 days, the yellowish gel was recovered by centrifugation and washed with distilled water. Because no template molecules were used, a further calcination step was not required. Through this process, amorphous silica nanoparticles assembled from primary particles of tens of nanometers were synthesized. Their surface area was 245 m$^2$ g$^{-1}$. Davarpanah et al. also used nitric acid for the titration of sodium silicate extracted from rice husk [65]. The pH of the solution was adjusted to 5.0, and the precipitated gel was aged for 24 h. Figure 2c shows that the obtained silica was irregularly shaped nanoparticles composed of 10 to 20 nm-sized primary particles. These morphological properties of precipitated silica particles have also been reported in previous studies using hydrochloric acid for pH adjustment [66–69].

The rise of environmental and safety issues has led to attempts to use organic acids instead of hazardous strong acids. In a study by Kalapathy et al., a silicate solution obtained from rice husk was titrated using citric acid or oxalic acid [70]. When the pH of the solution was adjusted to 4.0 or 7.0, amorphous silica was successfully obtained. In contrast to the case of using hydrochloric acid, no impurity peaks were observed in the XRD measurements. Moreover, no significant difference in the silica yields were observed regardless of the type of acid. The experimental results reported by Liou et al. showed that the silica particles produced by oxalic acid or citric acid exhibited higher yields than the silica particles produced by hydrochloric acid or sulfuric acid [33]. However, the residual sodium content in the silica particles was relatively high when citric acid or oxalic acid was used for
the precipitation reaction. The surface areas and pore volumes of silica produced by citric acid or oxalic acid were also lower than those of silica produced by hydrochloric acid (Figure 3).

**Figure 2.** (a) SEM and (b) TEM images of silica nanoparticles prepared under the optimum condition reported by Nassar et al. (reprinted with permission from [62]. Copyright 2019, Elsevier); and (c) SEM image of silica particles prepared by the titration of sodium silicate solution with nitric acid (reprinted with permission from [65]. Copyright 2019, Elsevier).

![Figure 2](image-url)

**Figure 3.** (a) Adsorption–desorption isotherm; (b) differential pore size distribution; and (c) BET (Brunauer–Emmett–Teller) surface area, pore volume, and extraction yield of silica samples prepared through various acid treatments (reprinted with permission from [33]. Copyright 2011, Elsevier).

**3.2. Control of Morphological Properties of Silica Particles**

Although the precipitation of silica by adding acidic reagents is a simple and convenient method, it cannot precisely control the morphological properties of silica. Most of the silica prepared by this approach exhibited irregularly shaped large particles assembled by small-sized primary particles. Therefore, advanced synthetic methods that can control the shape and surface properties of silica are required to apply rice husk-derived silica particles to modern industries. In this section, we review previous studies that used (i) organic co-solvents, (ii) polymer additives, and (iii) a water-in-oil emulsion system to control the morphology of silica particles.

Zulkifli et al. used ethanol as a co-solvent at the precipitation step of silicate [71]. In this study, sodium silicate solution extracted from rice husks was mixed with different amounts of ethanol. Then, the mixed solution was titrated with phosphoric acid. As a result, while irregular and highly aggregated particles were obtained without ethanol, dispersed spherical particles were synthesized with increasing amounts of ethanol. At the optimized condition (ratio of sodium silicate: $\text{H}_2\text{O}$:ethanol = 1:1:0.25 at pH 7), uniform silica nanoparticles with low aggregation were obtained, and their sizes...
ranged from 75 to 252 nm. The silica powders exhibited a BET surface area of ~364 m² g⁻¹. It was surmised that the formation of spherical particles originated from the formation of self-emulsion droplets consisting of silicate anions upon the addition of ethanol to an aqueous silicate solution [72]. A similar phenomenon was also observed in a study by Zulfiqar et al. [21]. The neutralization of the silicate solution with phosphoric acid in the presence of ethanol led to the formation of spherical silica particles. Furthermore, as the concentration of sodium silicate increased, the average size of silica particles precipitated at room temperature also increased continuously (Figure 4). Silica particles made from sodium silicate solution containing 0.7 wt % white rice husk (WRH) had a unimodal size distribution of 181 ± 17 nm. When the concentration of WRH in the sodium silicate solution increased to 5.6 wt %, the silica particles exhibited a tri-modal size distribution (352 ± 77 nm, 1.8 ± 0.3 μm, and 7.1 ± 1.3 μm). On the other hand, when the precipitation reaction progressed at 65 °C, the particle sizes decreased as the concentration of silicate solution increased.

The use of acetone, an organic solvent, has also been shown to be effective in producing spherical silica particles. Rajan et al. [73] added 40 mL of acetone to 100 mL of sodium silicate solution extracted from rice husk. Afterwards, the pH of the solution was adjusted to 7 using 5 M acetic acid. Through this optimized condition, they synthesized well defined spherical silica particles in the range of 200 to 400 nm.

Several studies have reported the synthesis of spherical silica particles using a polymer additive. In particular, the spherical shape control was achieved when polymers with sufficient ethylene oxide (EO) chains were used as additives [74–77]. It is considered that the interaction of the EO chains of polymers with the silicate species stabilizes the silicate during the solidification process, which leads to the formation of spherical particles [78]. In a study by Li et al., [74,75], they first dissolved polyethylene glycol (PEG, molecular weight = 20,000) in a sodium silicate solution. Then, by the titration of the silicate solution using phosphoric acid, spherical silica nanoparticles were obtained. Similar results were also reported by Le et al. [76]. When PEG (molecular weight = 10,000) was used as an additive, spherical silica nanoparticles could be obtained from the rice husk-derived silicate solution. On the other hand, by using a Pluronic P-123 polymer instead of PEG, Shahnani et al. prepared silica microspheres from a rice husk-derived sodium silicate [77]. A certain amount of Pluronic P-123 was dissolved in 2 M hydrochloric acid solution and then sodium silicate was added to the mixture. The overall reactions progressed under acidic conditions. After filtration and washing, the porous silica microspheres were obtained by calcination at 550 °C. The non-aggregated silica microspheres obtained by this process are...
shown in Figure 5. The silica microspheres had a BET surface area of 445 m$^2$ g$^{-1}$ and a pore volume of 0.298 cm$^3$ g$^{-1}$, respectively.

![Figure 5](image-url)

**Figure 5.** SEM images of the silica microspheres (reprinted with permission from [77], Copyright 2018, Elsevier).

The use of an emulsion system is a well known method for producing spherical particles. Hasan et al. reported a study that adapted this system for the preparation of spherical silica from a rice husk-derived silicate solution [79]. In the water-in-oil emulsion composed of water and toluene, cetyltrimethylammonium bromide (CTAB) and n-butanol were used as the surfactant and co-surfactant, respectively (Figure 6). After the formation of the reverse micelle, silicate was hydrolyzed by the urea at the micelle interface. The obtained silica particles exhibited a distinct spherical shape with a surface area and pore volume of 227 m$^2$ g$^{-1}$ and 1.24 cm$^3$ g$^{-1}$, respectively.

![Figure 6](image-url)

**Figure 6.** (a) Formation mechanism of silica sphere using Na$_2$SiO$_3$-RHA (rice husk ash) and CTAB (cetyltrimethylammonium bromide) in the water-in-oil emulsion system. TEM images of silica particles made from (b) commercial sodium silicate and (c) rice husk-derived sodium silicate (reprinted with permission from [79], Copyright 2018, Elsevier).
3.3. Synthesis of Ordered Porous Silica Particles from Rice Husk

Since a mesoporous aluminosilicate using a soft-template synthetic method was developed by the Mobil Oil Corporation in 1992 [80], numerous studies have been conducted to synthesize various types of ordered porous materials. In the case of silica-based materials, starting with the MCM (Mobil Composition of Matter) series, research on the development of various types of mesoporous silica, such as SBA (Santa Barbara Amorphous), KIT (Korea Advanced Institute of Science and Technology), FDU (Fudan University), and MSU (Michigan State University) series, have been conducted. At the same time, the requirement for cost-effective processes has led to the search for low-cost silica precursors that can replace silicon alkoxide reagents. This is one of the main reasons why rice husk-derived silicate has attracted attention as a raw material for the synthesis of mesoporous silica.

In the last decade, MCM-type silica has been successfully produced from rice husks in many studies. Conventional MCM-41 silica has a uniform hexagonal pore structure with a pore size of 2–4 nm. CTAB, a cationic surfactant, has been typically used as a structure-directing agent for MCM-41. CTAB forms rod-like micelles in the aqueous solution and aligns into a hexagonal array. The negatively charged silicate species above pH 10 preferentially interact with the positively charged surfactant heads. Accordingly, after the removal of the surfactant by calcination, mesoporous silica with a hexagonal pore structure was obtained. An example of the synthetic method in detail with reference to the reported paper is as follows [81]. First, considering the specific molar composition of SiO$_2$, NaOH, CTAB, and H$_2$O, a certain amount of CTAB was dissolved in distilled water. Then, this solution was added to the sodium silicate solution extracted from rice husk and stirred at 80 °C for 24 h. After the titration of the mixed solution using nitric acid to a pH of 10.0, it was aged for 48 h at the same temperature. The resulting gel was washed with distilled water and acetone, and subsequently calcined at 600 °C. Through this process, Ramalingam et al. synthesized MCM-41 silica particles using rice husk as the silica precursor (Figure 7); it showed a hexagonal pore structure with a monomodal pore size of 2.3 nm and a high surface area of 1115 m$^2$ g$^{-1}$ [81].

![Figure 7](image_url)  
**Figure 7.** (a) N$_2$ adsorption–desorption isotherm of rice husk ash-derived MCM (Mobile Composition of Matter)-41. The inset shows the corresponding pore size distribution; and (b) the TEM image of rice husk ash-derived MCM-41 (reprinted with permission from [81]. Copyright 2020, Elsevier).

Unlike MCM-41 silica, MCM-48 silica has a three-dimensional pore structure with cubic I$_{3d}$ symmetry. To obtain MCM-48 silica, the structure of the micelle formed by the self-assembly of surfactants must be changed. Several studies satisfied this condition by utilizing a cationic-neutral surfactant mixture system [82–84] or changing the surfactant concentration [85]. Subsequently, MCM-48 silica was successfully synthesized using sodium silicate solution extracted from rice husk. Looking at a specific example, Bhagiyalakshmi et al. used a mixture of CTAB and polyoxyethylene lauryl ether
(LE-4) as the structure directing agents [83]. Sodium silicate solution was added to the surfactant mixture (CTAB and LE-4) dissolved in an aqueous solution at 80 °C. Then, the mixed solution was titrated using acetic acid until the pH reached 10, and heated at 100 °C for 48 h. After filtration and washing, the final product was obtained by calcination at 550 °C. The obtained MCM-48 silica showed a bicontinuous I\textsubscript{a3d} cubic phase with a surface area of 1124 m\textsuperscript{2} g\textsuperscript{−1} and a main pore size of 3.9 nm. Morphological properties, such as the surface area, pore volume, and main pore size of the rice husk-derived MCM-41 and MCM-48 silica reported to date are summarized in Table 1 [81–95].

| Silica Type | Pore Diameter (nm) | Surface Area (m\textsuperscript{2} g\textsuperscript{−1}) | Pore Volume (cm\textsuperscript{3} g\textsuperscript{−1}) | Ref. |
|------------|-------------------|---------------|----------------|-----|
| MCM-41     | 2.9   | 800   | 0.93 | [86] |
|            | 2.86  | 943   | –   | [87] |
|            | 3.54  | 1101  | 0.96 | [83] |
|            | 3.51  | 1099  | 0.96 | [84] |
|            | 3.28  | 903   | –   | [88] |
|            | 2.3   | 1115  | 0.92 | [89] |
|            | 3.6   | 602   | 0.49 | [90] |
|            | 2.8–3.1 | 545–1210 | 0.36–1.00 | [85] |
|            | 2.92  | 797   | 0.57 | [91] |
|            | 3.16  | 1347  | 0.906 | [92] |
|            | 3.8   | 500.5 | 0.45 | [93] |
|            | 3.0–3.4 | 552–769 | 1.025–1.167 | [94] |
|            | 2.71  | 972.5 | 0.87 | [95] |
|            | 2.3   | 1115  | 0.92 | [81] |
| MCM-48     | 4.02  | 1024  | 2.58 | [82] |
|            | 3.89  | 1124  | 0.98 | [83] |
|            | 2.6   | 1059  | 0.68 | [84] |
|            | 2.5   | 815   | 0.75 | [85] |

Table 1. Pore diameter, surface area, and pore volume of MCM-type silica prepared from rice husk-derived silicate solution.

SBA-15 is one of the most common types of mesoporous silica and was first developed at the University of California [96]. SBA-15 has a two-dimensional hexagonal pore structure. Its pore size can be controlled in the range of 4–12 nm. It can be further increased up to 30 nm by using additional organic additives. One important feature of SBA-15 is that it has thicker pore walls compared to MCM-41. Thus, SBA-15 is more stable under high temperature and hydrothermal conditions [97]. In order to obtain SBA-15 having these advantages from low-cost raw materials, a number of studies using silicate extracted from rice husk have been reported. For the synthesis of SBA-15, Pluronic P-123, a nonionic triblock copolymer, is used as a structure directing agent. SBA-15 is assembled by the N\textsuperscript{0}\textsuperscript{H}\textsuperscript{+}\textsuperscript{X}\textsuperscript{−}\textsuperscript{I}\textsuperscript{+} mechanism, where N, H, X, and I indicate nonionic surfactant, hydrogen, halide, and silica source, respectively. Therefore, in difference with a case of MCM-41, the synthetic reaction proceeds under acidic conditions. Under these synthetic conditions, Henao et al. obtained SBA-15, which had a monomodal pore size of 7.6 nm with a high surface area of 604 m\textsuperscript{2} g\textsuperscript{−1}, from rice husk-derived silicate solution (Figure 8) [98]. Chareonpanich et al. synthesized SBA-15 from rice husk via an ultrasonic technique [99]; their SBA-15 exhibited a highly ordered hexagonal pore arrangement with a pore size of 9.5 nm. In the meantime, by using the Pluronic F-127 polymer instead of P-123, SBA-16-type silica was also successfully obtained from rice husk [100]. The obtained SBA-16 showed a three-dimensional...
cubic pore structure with a pore size of ~8.0 nm. The morphological properties of rice husk-derived SBA-type silica reported in previous studies are summarized in Table 2 [83,84,98–102].

![Figure 8](image-url)  
**Figure 8.** (a,b) TEM images of SBA (Santa Barbara Amorphous)-15-type mesoporous silica made from rice husk-derived silicate solution (reprinted with permission from [98], Copyright 2020, Elsevier).

| Silica Type | Pore Diameter (nm) | Surface Area (m² g⁻¹) | Pore Volume (cm³ g⁻¹) | Ref. |
|-------------|-------------------|------------------------|-----------------------|------|
| SBA-11      | 3.8/7.7/12.9      | 356                    | 0.792                 | [98] |
|             | 9.5               | 530–860                | 0.96–1.27             | [99] |
|             | 4.8               | 790                    | 0.82                  | [101]|
|             | 5.8               | 712                    | 0.68                  | [83] |
|             | 7.4               | 780                    | 0.95                  | [84] |
|             | 7.7               | 1095                   | 1.705                 | [102]|
|             | 7.6               | 604                    | 1.192                 | [98] |
| SBA-16      | 5.8–8.2           | 775–840                | –                     | [100]|

The synthesis of large-pore-sized ordered mesoporous silica from rice husk was reported by Chun et al. [103]. In this study, Pluronic P-123 and trimethylbenzene (TMB) were used as templates and pore expanders, respectively. Pluronic P-123, TMB, and rice husk-derived silicate solution were assembled in a neutral environment with the addition of acetic acid. Through the N[O] mechanism, amorphous silica with a well defined mesocellular foam structure was successfully obtained [104]. It has uniform mesopores with a size of approximately 30 nm and a large pore volume of 1.77 cm³ g⁻¹ (Figure 9a–c). Interestingly, when the concentration of sodium silicate extracted from rice husk increased, the usage of acetic acid increased to adjust the neutral pH, the pore size of silica was further expanded to approximately 60 nm (Figure 9d–f). The authors suggested that the large amounts of acetate promote the oxolation reaction and increase the hydrophobicity of silica, which led to the further pore expansion of silica [103,105].

Although they are not pure silica materials, several types of zeolites have also been synthesized using silicate extracted from rice husks. Zeolites are microporous aluminosilicate materials. Therefore, additional alumina resources had to be used for zeolite synthesis. Using rice husk-derived silicate and sodium aluminate reagent as a raw silica and alumina material, respectively, the synthesis of zeolite A [106], zeolite Y in sodium form (NaY) [107,108], ZSM(Zeolite Socony Mobil)-5 [109], ZSM-12 [110], ZSM-48 [111], and Linde Type J zeolite [112] have been reported in previous studies. The synthesis of various kinds of zeolite from the rice husk-derived silicate solution is covered in detail in a previous review [113].
The main components of rice husk—cellulose, hemicellulose, lignin, and inorganics—can be separated by their thermo-chemical properties. Acid leaching using a strong acid solution (e.g., H₂SO₄, HCl, and HNO₃) is effective to produce silica with high purity and surface area. However, these reagents are significantly hazardous to the environment and human life. Therefore, attempts to use environmentally harmless agents, such as citric acid and ionic liquid, have been reported.

Silica can be extracted from rice husk by solubilizing it in an alkali solution and precipitating in an acidic medium. In general, sodium hydroxide was used to extract silica from rice husk as sodium silicate.

The development of synthetic methods based on bottom-up processes enables the precise and uniform control of the morphological properties of silica products. These methods generally use a sodium silicate solution extracted from rice husks as a raw material.

The neutralization of sodium silicate solution using acid solution (e.g., H₂SO₄, HCl, HNO₃, organic acid) is a common method for the precipitation of silica particles. However, it is still not possible to accurately control the morphological properties of silica.
The use of (i) organic co-solvents (e.g., ethanol and acetone), (ii) polymer additives (e.g., PEG), and (iii) a water-in-oil emulsion system enables the control of the morphological properties, such as the shape and size, of silica particles.

Various ordered porous silica particles including MCM-type, SBA-type, and mesocellular foam structure have been successfully obtained from a rice husk-derived silicate solution with additional structure directing agents (e.g., CTAB, Pluronic P-123, etc.).

Based on these properties, they are expected to be utilized in potential value-added applications, such as heterogeneous catalysts, CO₂ capture, adsorbents for aqueous pollutants, biomolecular delivery, and cosmetic ingredients. The rice husk-derived engineered silica will further increase their value in modern society because they are manufactured from sustainable biomass resources.

For the practical use of engineered silica particles made from rice husks, several important issues must be addressed. As described in the previous chapter, the combustion of rice husks to remove organic components generates greenhouse gases and emits significant quantities of particulate matter. The use of strong acids to obtain high-purity silica is significantly hazardous to the environment and human life. Moreover, the overall synthesis procedure is complex, as shown in Figure 10a. As a result, the unit price of the final product is higher than those of silica particles made from mineral resources. We believe that overcoming these obstacles in the synthetic process is a prerequisite for the commercialization of engineered silica particles made from rice husks. One strategy for the preparation of rice husk-derived engineered silica through an environmentally friendly and cost-competitive process is proposed in Figure 10b. The direct extraction of silicate from rice husks using alkaline solution and thereafter titration using weak acids with polymer additives or co-solvents simplifies the overall process, while the use and emission of harmful substances can be minimized. However, the direct extraction of silicate using alkaline solution also leads to the extraction of organic components such as xylan. These organic components make it difficult to obtain engineered silica particles with high purity. Therefore, further research is needed to overcome these unresolved problems, and through this, it is expected that the commercialization of rice husk-derived silica will be one step closer.

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