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Biomass, Abundant Resources for Synthesis of Mesoporous Silica Material

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Additional information is available at the end of the chapter

Abstract

The synthesis of mesoporous silica materials was reviewed with a view to discuss the reaction mechanism and the various attempts made at enhancing the materials' properties by utilizing varieties of templating agents and silica frameworks from pure synthetic chemicals. This chapter also reviewed studies in which either the template or the framework was synthesized from benign reagents obtained from renewable sources, to achieve enhanced material properties. The view was to encourage the development of mesoporous silica materials in which both the template and the silica framework are from biomass origin. This approach may promote the large-scales synthesis of mesoporous silica for commercial purposes, which had previously been hampered by the toxic nature, cost of synthetic chemical reagents, and unsustainable synthetic routes.

Keywords: mesoporous silica materials (MSiM), templating agents, biomass, silica framework, micelle concentration, surfactant

1. Introduction

The facile discovery of M4IS family of mesoporous silica material is one of the significant breakthroughs in material science in the last two decades. This material with pore diameter between 2 and 50 nm has continued to be a subject of research focus till date, as its potential application in areas such as medicine, catalysis, adsorption, sensing, and photonics continues to rise. This is shown by more than 19,000 literature citations since 1993 along with numerous

patents on the subject matter annually. However, the large-scale commercialization of the numerous research findings and patents in these fields has not been feasible. This may be due to the high cost of reagents (surfactants and silica precursor) combined with environmental concerns occasioned by the high toxicity of majority of the surfactants and precursors system used in the synthesis. Thus, the large-scale synthesis of cheap and environmentally safe mesoporous silica material is one of the greatest challenges in modern material syntheses.

Recently, there have been renewed interests in mesoporous silica-based material synthesis fueled by the new synthetic approach which lay emphasis on the use of biologically derived materials found in nature or extracted from biomass resources. It is generally believed that the cost and the ecological impacts of these syntheses would be drastically reduced, thus increasing the possibility of commercialization [1] in the nearest future. In addition, these biosynthesized materials often have well-defined hierarchical structures/network and properties not hitherto seen in those synthesized via utilization of synthetic chemical reagents. Therefore, this chapter provides a critical assessment of the synthetic approach used in the synthesis of mesoporous silica materials with a view to encourage biomass utilization as potential feedstock for the synthesis if scale-up development of mesoporous silica materials is envisioned at reasonable cost and with relatively less impact on the environment.

The review is organized into four sections. Section 2 reviews the background into the synthesis of mesoporous silica material (MSiM) from commercially sourced reagents (surfactants and silica framework) with a view to provide insight into the effects of choice of reagents on the structure and characteristics of the synthesized materials. While Section 3 focuses on the progress made in the part utilization of biological/biomass materials and the effects on their inclusion on pore size, surface area, and morphology in comparison with materials derived from purely synthetic chemicals. Finally, Section 4 emphasizes on the view to maximize the potential of biomass waste materials in advanced material synthesis.

2. Mesoporous silica synthesized by liquid crystal templating approach

2.1. Background into the synthesis of MSiM from conventional reagents

Mesoporous materials, an upper pore extension of microporous zeolithic materials, have attracted much attention due their large surface area (>1000 m^2/g), pore volume (app. 1 g/cm^3), and narrow pore distribution that can be adjusted between 2 and 50 nm to meet specific needs and functions. The commercial interest in their applications in catalysis, photonics, sensing, chiral separation, and drug delivery are additional incentives to focus on their synthesis. Pioneered by the facile discovery of the M4IS family (including MCM-41, MCM-48, and MCM-50) of mesoporous materials in 1992 [2]. The synthesis of MCM-41, the first and most popular member of the M4IS family, was facilitated by assembly of long chain cationic surfactant into micelles or lyotropic liquid crystals (LCC) at a specific surfactant concentration in aqueous solution known as *critical micelle concentration* (CMC). Hexadecyltrimethylammonium ion, a cationic surfactant, was used as the template-forming agent. These amphiphilic molecules assembled in polar solvents forming a hexagonal array of cylindrical micelles in which the non-polar hydrophobic water-

repelling tail gathered in the centre and the polar hydrophilic water-loving head on the surface. This micelle served as template or pore-forming agent for the subsequent sol-gel hydrolytic polycondensation of inorganic silicate precursor, an alkoxysilanes (such as tetraethyl orthosilicate) under hydrothermal conditions in solution [3], forming an organic-inorganic composite. When the composite is calcined, the template is removed leaving the porous network. But earlier in 1990, Yanagisawa et al. [4] obtained a material which was later designated as folder sheet mesoporous materials (FSM)-16 by intercalating kane-mite, a layered silicate with organic alkyltrimethylammonium chloride, a cationic surfactant. During the interaction, the SiO_2 layers in the organic-kanemite complexes were con-densed to form 3-D SiO_2 networks which upon calcination yielded products having pores diameter 2–4 nm and large surface area (ca. 900 m^2/g). However, at the time of the publication, the materials were thought to be microporous as a mixed phase of surfac-tant and precursor was obtained.

In the report of Beck et al. [2], self-assembly and electrostatic charge matching between the surfactant and inorganic precursors was believed to be the driving force for the formation of mesostructure. Later, Tanev and Pinnavaia [5] reported a new approach to the synthesis of mesoporous materials via a neutral surfactants-templating approach which complemented the ionic-dependent pathways. This approach is based on hydrogen bonding and self-assembly between neutral amines and neutral inorganic precursor at ambient temperature. Due to weaker repulsive interaction between the neutral surfactant and precursor at the surfactant-solution interface, structures with thicker framework walls, small scattering sizes, and textural mesoporosities matching with those of materials produced from ionic pathways were ob-tained. The thicker walls supplied the material with improved thermal and hydrothermal stability and also made the environmentally benign recovery of the template via solvent extraction possible. In addition, the most significant chemical advantage of this approach perhaps is the synthesis of materials that cannot ordinarily be assessed by ionic templating approaches (e.g., alumina). In spite of the obvious advantages of the neutral templating route over the ionic route, the neutral surfactants still suffer from the same negative aspect as the cationic quaternary ammonium surfactants such as high cost and toxicity are therefore not suitable for large-scale syntheses of mesoporous materials. The original neutral templating approach was extended to obtained phases with increased wall thickness and thermal stability by the use of block copolymers (BCs). BCs such as the polyethylene oxide (PEO) polymeric surfactants were used for the synthesis of disordered worm-like phases at neutral pH and triblock copolymers under acidic condition to obtain highly ordered 2-D Santa Barbara Amorphous (SBA). However, despite the low cost of BCs, the surfactant showed poor degradability and toxicity to organisms, thereby hindering its utilization in large-scale syntheses.

2.2. Synthetic pathways

Several investigations into the synthesis of mesoporous silica materials have concluded that two different mechanisms are involved: (a) On the one hand, it involved the self-assembly of the surfactant (at high concentration) into a lyotropic crystalline phase (micelles) independent

of the crystallization and subsequent polymerization of the silica framework around the preformed micellar aggregates framework. (b) On the other hand, it is also possible to produce this phase at lower surfactant concentration; the cooperative self-assembly of the surfactant and inorganic species is directed by the aqueous inorganic silica precursor to obtain liquid crystalline phase with hexagonal, cubic, or lamellar shape (**Figure 1**)
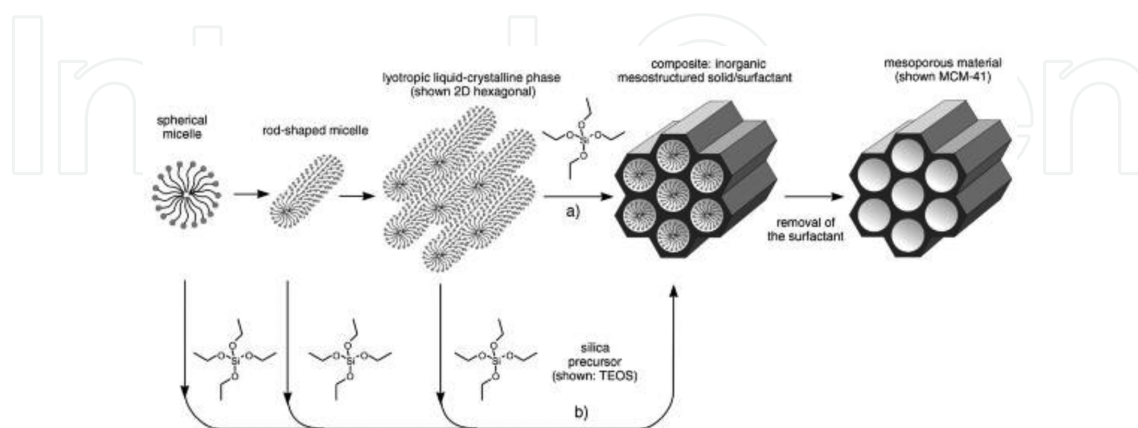

Figure 1. Formation of mesoporous materials by surfactant structure directing agents: (a) true liquid-crystal template mechanism, (b) cooperative liquid-crystal template mechanism [2].

A basic condition for the mesophase formation is that there must be an attractive interaction between the template and silica precursor which guarantees the subsequent inclusion of the structure-directing agent (SDA) in the final material without the occurrence of phase separation. According to Huo et al. [6] these interactions can be classified as follows: (a) under basic conditions, where the silica species are present as anions and cationic quaternary ammonium surfactants are used as the SDA, the synthetic pathway is termed (S^+I^-). (b) The original synthesis of MCM-41 is based on this pathway. In the charged reversed phase, under acidic conditions (i.e., below the isoelectronic point of the silica species; pH = 2) where the silica species are positively charged, an anionic SDA (S^-) is used to direct the self-assembly of cationic inorganic silica species (I^+) through the S^-I^+ pathway. (c) To produce an interaction with the cationic surfactant, a mediator ion X^- (usually halides) may be added to direct the mesophase formation via the $S^+X^-I^-$. (d) Conversely, when negatively charged surfactants (S^-) are used, it is also possible to work under basic condition whereby a mediator ion M^+ (usually alkali ions) can be added to ensure interaction between equally negatively charged species via $S^-M^+I^-$ pathway. Therefore, the interactions in pathways (a)–(d) are predominantly electrostatic in nature. In addition, it is possible for the attractive interactions to be mediated by hydrogen bonds; this is the case when neutral (S^0, e.g., long-chained amine) or nonionic surfactants (N^0, e.g., polyethylene oxide) and uncharged silica species (S^0I^0 or N^0I^0) or ion pairs (S^0H^+) (X^-I^o) pathways are present.

Depending on the nature, concentration, and temperature, surfactants in lyotropic systems can form different liquid crystal phases which includes isotropic micellar, cubic micellar, lamellar, or reversed-phase micellar phases. Therefore, the behavior of surfactants is the key for the controlled synthesis of silica mesostructure. As proposed by Israelachvili et al. [7], the relative

stabilities of the different micellar aggregate shapes and the mesophase structures can be predicted from a combination of molecular packing considerations and general thermodynamic principles. He further states that the preferred shape of the self-assembled surfactant molecules above its CMC depends on the effective mean molecular parameters of the micelle that establish the value of a dimensionless packing parameter g, which is defined as $g = V/a_o l_c$, where V is the effective volume of the hydrophobic chain, a_o is the mean aggregate surface area per hydrophilic head group, and l_c is the critical hydrophobic chain length [7]. The parameter g depends on the molecular geometry of the surfactant molecules, such as the number of carbon atoms in the hydrophobic chain, the degree of chain saturation, and the size and charge of the polar head group. In addition, the effects of solution conditions including ionic strength, pH, co-surfactant concentration, and temperature are included in V, a_o, and l_c.

3. Utilization of materials from renewable biomass as alternative reagents

Different processing parameters such as the type of surfactant and precursor among others determine the porosity and morphology of the final material. Mesoporous materials have been largely synthesized from synthetic/commercially sourced surfactants and precursors. However, the high cost, toxicity, and environmental impacts of these reactants and syntheses have led to the search for alternative functional replacements and environmentally benign synthetic routes. Recently, biomass, a renewable resource, has been identified as an abundant source of diverse surfactant materials such as polysaccharides, polypeptides and polyaromatics, and silica frameworks (from rice husk, wheat husk, etc.) that could be applied in silica mineralization. Many biomass materials exhibit hierarchical large-scale order and self-assembly properties that can be replicated in a variety of structures; hence, the use of biomass materials as alternative to commercial surfactants and precursors not only yields materials with structural diversities but also holds promise for the synthesis of low-cost completely biocompatible materials with reduced toxicity and application in areas of human medicine.

3.1. Utilization of surfactants derived from biomass resources

In the last few years, several efforts have been made in the production of surfactants with low toxicity and biodegradability; this includes the use of surfactant building blocks (hydrophilic/polar head and hydrophobic tail) derived from renewable resource and the use of surfactants derived from renewable polymer- and colloid-based biomacromolecules such as cellulose and chitosan. With respect to renewable hydrophobic segment of the surfactant, natural fats and oils, which are composed of wide distribution of fatty acids, have been applied in the synthesis of mixtures of surfactants. One of the limitations associated with the use of templates/SDA derived in material synthesis is that they are often obtained in mixtures containing anionic surfactants. The challenge here is that each of the components may interact differently with the silica precursor preventing a suitable organization of the porous network. Moreover, their purification may lead to increase in cost as well as adverse environmental impacts. However, the advantage inherent in this approach is the abundant availability of this sources and their fast biodegradability.

Canlas and Pinnavaia [8] reported the utilization of naturally derived oleyl amine surfactants for the synthesis of worm-like and lamellar mesoporous silica. These structures are similar to those obtained using petroleum-based alkyl amine surfactant via the S^0I^0 templating mechanism thus showing that surfactants from renewable source could effectively be used as templates in mesoporous silica synthesis. However, at lower solvent polarity, the surfactant, due to the flexibility of the hydrophobic chain, adopted a hairpin and other extended structures generating mesoporous silica with pore size in the supermicroporous range, thus making them more flexible as templating agents than the alkyl amines. This supermicroporous derivative is believed to offer greater size and shape selection separation and catalysis in comparison to their mesoporous analogues. Oleyl amine is obtained by the transformation of oleic acid derived from tallow fats or vegetable oils such as soya or palm oil. With respect to utilization of hydrophilic segment from renewable resource in generating eco-friendly surfactants, amino acid derived surfactant from another interesting group of renewable surfactants known for their excellent surface activity, biocompatibility, and low toxicity. Thomas et al. [9] reported the use of surfactant formulations based on glutamic acid and leucine containing a mixture of lauronyl amino acid and fatty acid as SDA for the formation of mixtures of ordered mesoporous silica including lamellar phases. This approach was challenging as the synthesis was carried out at neutral pH and room temperature using organic and inorganic reactants from renewable sources. Measurement of amino acid-based SDA CMC, surface tension at CMC (ST), foaming capacity, and foaming stability showed that the surfactant mixtures with the longest chain have properties comparable to petroleum-based surfactants [10]. Sodium N-dodecyl glycine ($C_{12}H_{25}NHCH_2COONa$) and potassium N-dodecyl glycine ($C_{12}H_{25}NHCH_2COOK$) amino acid-based surfactants prepared by reacting coconut oil amine with monochloroacetic acid in alkali medium were used to synthesize mesostructures different from lamellar, more precisely the synthesis of hexagonal and Pm3n cubic structures [11].

Another interesting class of surfactant with polar groups derived from renewable resources is the alkyl glycosides with growing interest due to their liquid crystalline phase-forming ability, chiral properties, non-toxicity, and biodegradability. Alkyl glycosides are another class of surfactants with polar head derived from renewable resources. The development of well-ordered materials using this sugar-based nonionic surfactant is however limited because the interaction between the weakly charged inorganic silica precursor and the nonionic surfactant are short-ranged hydrogen bonding often resulting in disordered mesostructure. The deposition of mesostructure silica films via the self-assembly of commercially available sugar-based alkyl glycosidic nonionic surfactants, such as n-octyl β-D-glycopyranoside (β-C_8Glc), n-dodecyl β-D-maltopyranoside (β-C_{12}Mal), and n-decyl β-D-maltopyranoside(β-C_{10}Mal), in combination with a prehydrolysed silicate, and the effects of size of sugar head group and alkyl chain length on the type of supramolecular assembly of the surfactant have been reported [12]. Although the three alkyl glycoside surfactants were successfully utilized in the sol-gel processing of crack-free mesoporous silica films, the hydrogen bonding interactions with the silicate species during the gel formation suppressed the siloxane condensation. β-C_{10}Mal and β-C_{12}Mal with bigger maltose head group formed curved mesophases at lower concentrations and lamellar phases at higher concentrations that were stable to template removal by solvent extraction or calcination. β-C_{12}Mal-templated and β-C_{12}Mal-calcined

mesostructure silica film exhibited a significantly higher d spacing (41 Å) than the corresponding β-C$_{10}$Mal-templated silica (30 Å).

Renewable biomass wastes generated by agro-processing and food industries, including polymers and polymer colloids belonging to the polysaccharide family, constitute a potential field of research for obtaining new sustainable surfactants for the design of functional mesostructure. This is due to their availability, non-competitive use in the food industry, and more importantly, the rich chemical functionality and easy formulations [13]. Various polysaccharide-based polymers have been used as templates to direct the synthesis of silica; these include chitosan and chitin colloids and cellulose. Chitin, which is found in the exoskeletons of crustaceans, mollusk, and insects in nature, is the second most abundant renewable polysaccharide in nature. However, its use in design of functional material is limited by its poor solubility, but on partial deacetylation, it yields chitosan, a water-soluble substance furnished with several free amino acid groups. Due to its solubility in acidic media and its rich chemical groups, chitosan has been used for structuring silica-based materials [13–15]. However, these efforts yielded poorly ordered materials after template removal by calcination.

Recently, Alonso and Belamie [16] presented a versatile and novel approach involving the use of chitin colloids ($L = 260 \pm 80$ nm, $D = 23 \pm 3$ nm) from shrimps which are made up of bundles of chitin nanorod ($D = 3.2 \pm 0.6$ nm) with amino groups on their surface. The mechanism of formation is governed by the chitin nanorods self-assembly coupled with chitin-siloxane soft attractive attractions, which bore similarities with cooperative and dynamic template mechanisms proposed earlier [17, 18]. Nguyen et al. [19] reported the ordering of mesoporous silica with high surface area and layered structure templated by chitin nanocrystals (ChNCs) derived from king crab shell waste. ChNCs are spindle-shaped aqueous suspension of chitin nanorod prepared by sequential deacetylation and hydrolysis of chitin [20]. The ChNCs self-assemble into a nanocrystalline liquid crystal phase (NLCP) which was used to template silica. Removal of template yielded a crack-free mesoporous film with layered features that originated from the nematic organization of the ChNCs.

Cellulose is the most abundant natural biopolymer, which is renewable, biodegradable, and non-toxic. It is a polysaccharide composed of monomeric anhydroglucose units connected by β-1,4-glycosidic bonds. Cellulose also exhibits self-assembly properties and an inherent structural hierarchy. It is considered as a green alternative to petroleum-based polymers commonly used as template for the fabrication of mesostructured silica phases. When subjected to acid hydrolysis, cellulose nanocrystals (CNCs), a colloidal suspension, containing the crystalline portion of the polysaccharide, have been reported to assemble into nematic liquid crystalline phase (NLCP), is obtained [21]. This entity, CNC, has been used as a renewable and inexpensive template to cast hybrid mesophase in material synthesis. Dujardin et al. [1] reported a novel synthetic approach to the synthesis of mesoporous silica which involved the sol-gel mineralization of partially ordered suspension of nematic liquid crystalline CNC template. Removal of the CNC template by calcination at 400°C produced a cracked birefringent silica matrix with pattern mesoporosity consisting of co-aligned cylindrical pores of approximately 15 and 9 nm diameter and wall thickness, respectively. Significant extension in pore length far beyond the length of individual CNCs were found

to be suggestive of both lateral and lengthwise close packing in the nanocrystal bundles of the nematic template.

The versatility of use of cholesteric phase of cellulose derivatives was demonstrated by Thomas and Antonietti [22] with the use of NLCP of hydroxypropyl cellulose for the generation of a porous silica with high surface area devoid of long-range chiral organization of the template. A freestanding mesoporous silica with high surface area that is a cast of a chiral nematic liquid crystal formed from CNC was reported by Shopsowitz et al. [23]. It was the first material to combine mesoporosity with long-ranged chiral ordering that showed photonic effects. Recently, mesoporous KIE-6 (Korea Institute of Energy-6) was synthesized using crude glycerol waste (CGlW) from biodiesel production. Biodiesel is synthesized through the trans-esterification of triglycerides from biomass such as palm and jatropha; about 1 million tons of CGlW is generated annually. CGlW (consisting of water and methanol, 40%, and glycerol, soap, and fatty acid methyl ester (FAME), 60%) waste constitutes an environmental problem because it is eliminated by incineration, releasing green house gases into the environment, as the cost for its purification is high. Hence, its use in the synthesis of porous material is a solution to its disposal. The glycerol/silica composite with tunable pore size, pore volume, and specific surface area was synthesized by adding glycerol waste and sulfuric acid into the silica sols at room temperature. However, a pre-calcination step at 150°C for 2 h was introduced to prevent the escape of the pore-forming glycerol before the formation of a rigid network by silanol group condensation. Otherwise, glycerol is evaporated before condensation resulting in reduced pore size and volume in the calcined composites. The CGlW template was removed by calcination in air at 550°C for 2 h yielding a 3-D interconnected worm-like mesoporous KIE-6. Properties of mesoporous KIE-6 such as specific surface area, pore size, and volume, and silica wall thickness were tuned by varying the crude glycerol concentration. Variation in glycerol: silica weight ratio in the composite from 0 through 4.9 to 8.0 yielded composites with increased pore size of 4.7 nm through 7.2 and 10 nm, respectively; pore volume from 0.53 to 1.01 cm^3/g and stable Brunauer-Emmett-Teller (BET) surface area between 443 and 550 m^2/g. In addition, life cycle assessment (LCA) of all the indexes included in the synthetic process from biomass cultivation, through biodiesel production to synthesis of mesoporous material, showed that CO$_2$ emitted during KIE-6 synthesis was much lower than in other existing routes for mesoporous silica. The reduction was attributed to the utilization of renewable CGlW. A major drawback in this synthetic approach, however, is the inclusion of methanol in the CGlW [24].

3.2. Utilization of silica frameworks from biomass residues

Rice, grasses (Germinaecea: bamboo, wheat, maize, and oats), sedges (Cyperaceae), and horsetails (Equisetums) are known to contain high concentration of biogenic silica. Silica is believed to be absorbed from the large abundance of silica in the earth crust released by geological processes as water-soluble silicic acid, Si(OH)$_4$, which through subsequent polymerization and precipitation are deposited as extracellular deposits on cell walls. This process is known as biosilicification. Biosilicification occurs under mild conditions, generating a variety of complex and hierarchical nanostructures silica frameworks which contributes to cell

wall rigidity, photosynthesis efficiency, and increased resistance to pathogenic attacks and diseases [25]. Rice husk (RH), which is currently the main natural silica producer, is a waste generated by rice milling activities and this accounts for 20–25 wt% of the whole dried rice grain. According to the United Nations Food and Agriculture Organization [26], the world rice production in 2014–2015 was estimated to be around 740.2 million tons. Therefore, RH makes up about 20 wt%; rice husk waste is a vast silica source. Due to their characteristic woody and abrasive nature, great bulk, slow biodegradability, and low nutritive properties, efforts made to utilize RHs have been very limited. These involve the pre-treatment of the RH to increase its surface area, decrease crystallinity of cellulose, eliminate hemicelluloses and break the lignin seal [27]. RH is generally removed by burning to yield particulate rice husk ash. RHA, containing nearly 90% silica and other metallic oxide as impurities, is commonly used raw materials for obtaining highly pure silica [28]. Trace metallic impurities in RHA silica have been found to be responsible for the clustering of primary silica nanoparticles (Nps). These metallic cations such as K^+ promote the melting of silica Nps and their concentration are responsible for different degrees of melting and different pore structures and pore sizes (**Figure 2**) [29]. Several reports on the extraction of pure biogenic nanosilica from RHA have been published [30–33]. However, before its utilization, a preliminary purification step is required to remove its constituent metallic oxides impurities. After calcination to eliminate the organics, metallic impurities such as oxides of alkali metals are removed by leaching with NaOH solution at temperatures between 100 and 200°C for 1 h. Direct recovery of silica by precipitation from the basic solution is achieved by addition of drops of sulfuric acid to the hot basic solution, followed by thermal treatment at 110°C [34]. Several products of commercial interest such as silicon carbide (SiC) used as semiconductors, pozzolan in cement manufacturing, and recently, sodium silicate in the preparation of silica-based mesoporous materials have been reported [35–42].
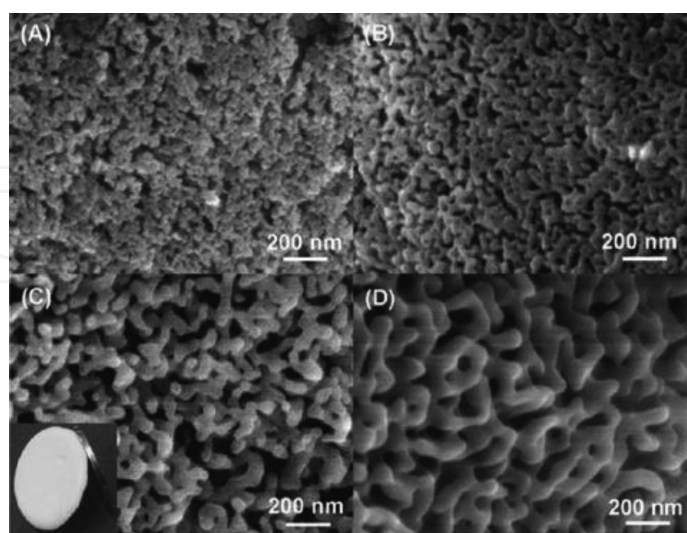

Figure 2. SEM image of nanoporous silica: (A) 0.20 M K^+ pyrolysis at 800°C for 2 h; (B) 0.20 M K^+, pyrolysis at 800°C for 4 h; (C) 0.20 M K^+, pyrolysis at 800°C for 8 h; (D) 0.50 M K^+, pyrolysis at 800°C for 8 h. Effect of K^+ on mesoporous silica from bagasse ash [29].

Siriluk and Yuttapong [42] demonstrated that RHA silica generated from biomass power plant can be used as silica framework for synthesis of MCM-41-type material with crystallinity characteristics and porosity similar to those synthesized from commercial silica. Some authors have reported the synthesis MCM-41-, MCM-48-, and SBA-15-type materials on which functional entities were grafted on the surface silanol groups using sodium silicate solutions extracted from RHA [36, 37, 40]; their potential for CO_2 and chlorinated volatile organic molecules adsorption was found to be similar to those synthesized from conventional silica sources. Recently, Rahman et al. [43] synthesized mesoporous silica with controlled pore structure from bagasse ash with approximately 656 m²/g surface area and pore diameter 18 nm. Pore structure was influenced by the presence of Na^+, template concentration, and pH.

4. Options to explore the use of both templates and precursors from renewable resources

Several attempts have been made to employ inexpensive, non-toxic, and renewable biomaterials in synthesizing "*green*" porous materials, as the potential of these materials are now being recognized [44]. This is achieved by the extraction of template from biomass and infiltrating it with aqueous inorganic species in solution followed by calcination to remove the template. This approach has been applied in the synthesis of metal carbide replica such as SiC and ZrC [44]. The inherent complexities of organic components present in biological microstructure of biomass after the removal of the inorganic have been employed to create hybrid replicas, thus modifying and enhancing the properties of calcined hybrid material via incorporation of features (such as high surface area, porosity, and even cellular functions) of the biological structure. Ogasawara et al. [45] synthesized ordered porous silica-chitin composite, using well-organized β-chitin organic matrix replica of the chamber-like architecture of cuttlebone. The demineralization of the cuttlebone produced a white organic matrix in which the 3-D chamber-like architecture of the cuttlebone was preserved. Treatment of the cuttlebone template in a sodium silicate solution at pH 11.5 followed by reaction in a series of ethanol-water mixture between pH 10 and 10.5 yielded a porous replica with 3-D interconnected box structures. Witoon et al. [15] reported the synthesis of a bimodal porous silica (BPS) with wormhole-like mesopore with large surface (783 m²/g), large total volume, high thermal stability, and tunable pore diameter (3.4–14 nm) from low-cost RHA sodium silicate and deacetylated chitosan as template. The organization and particle size in BPS were found to increase with the increase in pH. Materials with wormhole-like mesopores and macropores were obtained, respectively, at pH 3 and 5 after template removal by calcination. This is due to the increasing solubility and condensation rate at increasing pH and the fact that degree of hydrolysis of the silicate species is at very minimum close to neutral pH, thus forming larger silica particles [46]. A lot of opportunities to synthesis porous materials abound in the environment, particularly those involving the utilization of waste materials. This would without doubt, enhance the value of these wastes as well as proffer a solution to the menace caused by their disposal.

5. Conclusion

The synthesis of mesoporous silica material from commercially available templates and silica frameworks has made the large-scale production of this material unrealistic. This is due to high cost and the negative environmental impacts of the reagents and the harsh synthetic conditions. Recently, attempts have been made to utilize alternative reagents from renewable sources and benign synthetic routes. However, these efforts have largely been directed toward the part utilization of renewable biomass materials as reagents at near neutral pH. Although the materials derived showed characteristics and properties that are similar to those synthesized from commercially available reagents, efforts directed to the full utilization of renewable reagents belittle this fact. Therefore, there is need to focus attention on the full utilization of renewable biomass-generated reagents in the synthesis of MCM. This approach will not only result in the low-cost production of less toxic materials that will be suitable for various applications but also proffer solutions to the environmental and health threats associated with sustainable biomass waste removal.

Acknowledgements

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