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Mesoporous Materials Prepared Using Cashew Nut Shell Liquid and Castor Oil as Surfactants

James Mgaya and Egid Mubofu

Abstract

Preparation of useful materials using renewable resources, which are not in competition with food production is of particular importance in the current efforts to replace non-renewable resources. One example of a potential renewable resource, which is attracting the attention of researchers in the preparation of useful materials is cashew nut shell liquid (CNSL). CNSL which is a by-product of cashew processing factories, is a mixture of four potential compounds, namely anacardic acid, cardanol, cardol and 2-methyl cardol. Among other potential applications, cashew nut shell liquid is a good template source for preparation of mesoporous materials. Heterogeneous catalysts prepared using CNSL templates are more efficient than those prepared using the commercially available templates. The pore sizes of mesoporous materials prepared using CNSL templates are large (up to 25 nm) enough to immobilize enzymes. Another renewable resource; castor oil, has also been reported to be a good template source for preparation of mesoporous materials. This chapter therefore is aimed at describing in detail the preparation, characterization and applications of mesoporous materials templated by cashew nut shell liquid and castor oil.

Keywords: cashew nut shell liquid, castor oil, micelle templated silica, heterogeneous catalysts, bio-catalysis

1. Introduction

1.1 Mesoporous materials

According to IUPAC, porous materials are divided into three classes, namely microporous (with a pore diameter below 2 nm), mesoporous (2–50 nm), and macroporous (larger than 50 nm) materials. The discovery in 1992 by Mobil researchers [1, 2] of the meso-structured MCM materials obtained by self-assembly of surfactants in aqueous solutions and silicates or aluminosilicates was one of the major breakthroughs in material science. Such materials have found great utility in sorption media, biosensors, biomedical and catalyst applications due to their large internal surface area. Their high density of silanol groups on the pore walls is beneficial to the introduction of functional groups with high coverage. One of the methods to synthesize mesoporous materials is to use a surfactant-templated sol-gel system [1, 2]. In the sol-gel technique, one starts with an appropriate alkoxide such

as tetramethyl orthosilicate (TMOS) or tetraethyl orthosilicate (TEOS), which is mixed with water and a mutual solvent, such as ethanol or methanol, to form a solution, and the hydrolysis of the silicate leads to the formation of silanol groups, Si—OH. As the hydrolysis and condensation reactions (**Figure 1**) continue, viscosity increases until the sol ceases to flow and form the gel.

These silica materials prepared using sol-gel reactions with micelle templates are generally called micelle templated silica (MTS). The silica surface display different types of Si—O bonds, either silanols (≡Si—OH) or siloxanes (≡Si—O—Si≡), which have important influence on the particle properties.

1.2 Cashew nut shell liquid (CNSL) and castor oil as green templating agents

The general synthesis strategy of micelle templated silica (MTS) involves the condensation of an appropriate monomer in the presence of a templating agent (**Figure 2**). The templating agent is later removed from the composite material by soxhlet extraction, hot filtration or calcinations revealing a network of pores [3–5]. Surfactants are the commonly used template sources in the synthesis of micelle templated silica materials. They are amphiphilic compounds (usually organic compounds), which means they contain both hydrophobic groups (their tails) and hydrophilic groups (their heads). As a result of their amphiphilic nature, surfactants form aggregates (self-assemble) in solution mostly due to the hydrophobic effect. In the resultant aggregates, the amphiphilic molecules are arranged such that their hydrophobic groups are shielded from the aqueous medium by the polar head groups [6]. In dilute solution, surfactant molecules exist as monomers, but organize spontaneously into micelle when their concentration exceeds the critical micellar concentration [7]. Surfactant self-assembly (micelle) directs the organization of inorganic and organic precursors via non-covalent interactions: electrostatics, van der Waals, hydrogen bonding and π-π interactions.

The structure of the components of CNSL (cardanol, anacardic acid, cardol and 2-methyl cardol) contains polar phenolic part and non-polar 15 carbon alkyl non-polar chain which makes CNSL a suitable surfactant for preparation of mesoporous materials [8]. Likewise, the presence of carboxylic and hydroxyl groups in ricinoleic acid (which is a major component of castor oil; 90%) makes it an amphiphilic
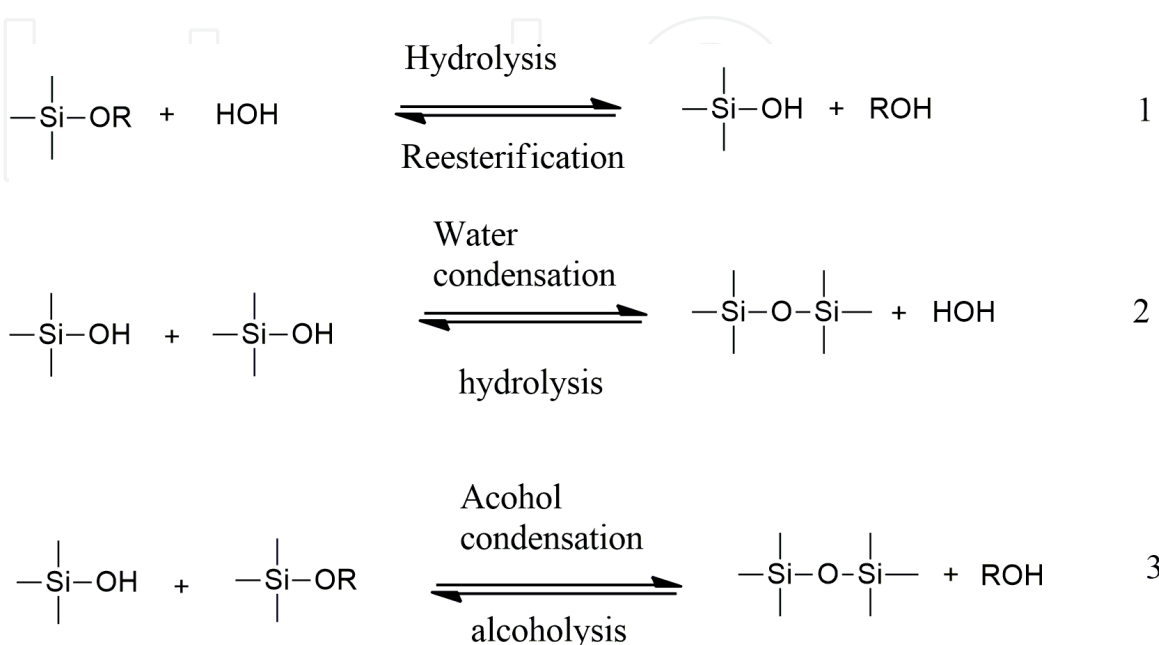
Figure 1.
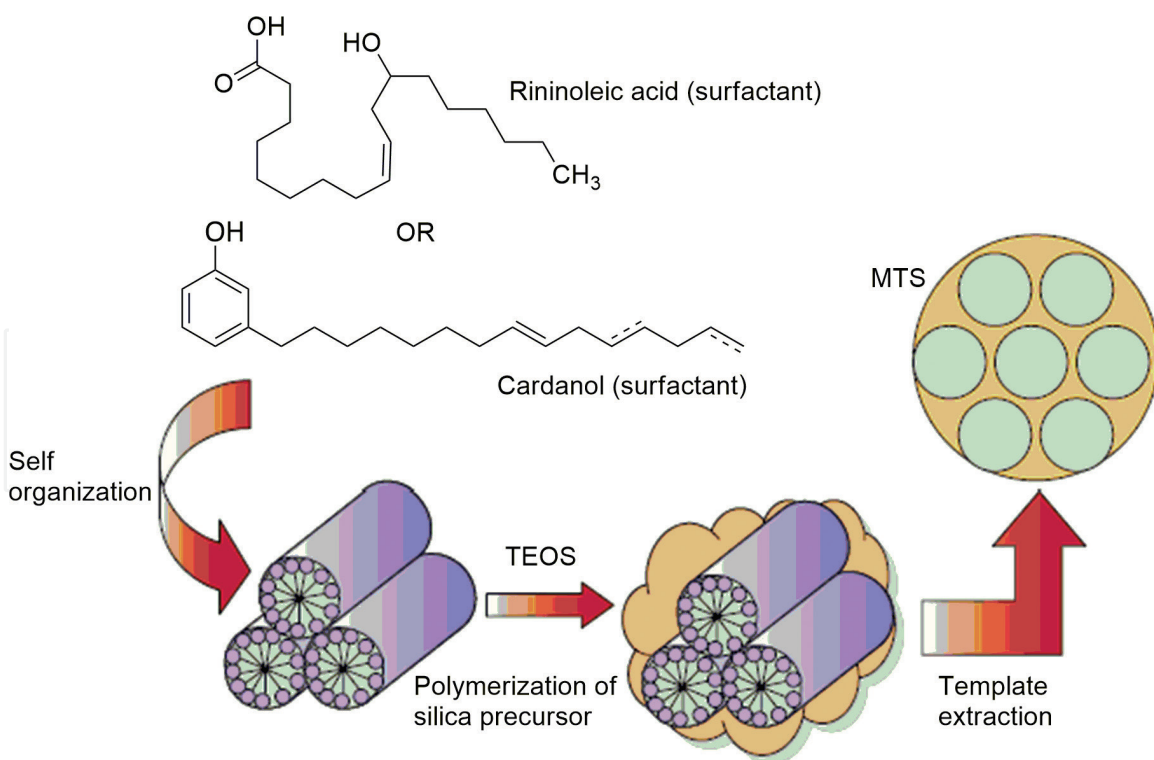*Sol-gel reactions for the formation of silica gel.*

Figure 2.
Formation of micelle templated silica using CNSL and castor oil templates.

molecule in which the polar head is comprised of carboxylic acid and hydroxyl groups, while the rest of the carbon chain constitutes a hydrophobic tail. The amphiphilic nature of ricinoleic acid qualifies the castor oil as a source of micelles (template) for the synthesis of mesoporous materials.

The most commonly utilized groups of surfactants are the quaternary ammonium salts [9], the neutral amines [10] and the block copolymers [11]. It is proposed [12] that neutral surfactants direct formation of mesophase through hydrogen bonding interactions and self-assembly between neutral amine micelles and neutral inorganic precursors while charged surfactants involve electrostatic interactions. For the quaternary-derived materials, it is very difficult to remove the template in such a way that it can be recovered. In contrast, the removal of neutral surfactants (amines and polyesters) is very simple. The relatively weak interactions between the template and the wall of the material (hydrogen bonding) can be broken easily by heating in hydrogen bonding solvents such as ethanol and the template can be recovered completely, leaving behind the inorganic framework and a solution of the template [13], hence, this is the greenest way to produce mesoporous materials. Castor oil and CNSL are environmentally friendly and biocompatible neutral surfactant that have proven (as discussed in the next sections) to be potential replacement of commercially available surfactants which most of them are not environmentally friendly. Successful preparation of mesoporous silica materials using CNSL templates is one of great contributions of knowledge considering the fact that science has taken a new direction of research into using renewable raw materials in making industrial chemicals.

2. CNSL templated mesoporous silica materials (CNSL-MTS)

CNSL-MTS materials with functionalized surfaces for various applications can be prepared by either one pot co-condensation method or grafting method (also known as postsynthetic method). In co-condensation (direct or one-pot) synthesis,

a condensable precursor bearing the desired functional group is added to the mixture containing the components for the formation of the mesoporous silica. In the postsynthetic method, the functional group is introduced after the formation of the mesoporous silica, either before or after removal of the template [14]. The one pot co-condensation method is the commonly used method of preparation of CNSL templated mesoporous materials. The synthesis is done by adding CNSL (surfactant) into a stirred aqueous ethanol (solvent) at ambient conditions of temperature and pressure. To this solution, TEOS (silica source) and a functionalizing agent (example; APTMS) are separately but simultaneously and rapidly added (in a ratio of 1:4 or 1:9). After 18 h, the resulting thick paste is vacuum filtered, thoroughly washed with ethanol. The template is removed by Soxhlet reflux using ethanol as a solvent for 10 h. The final solid (MTS) is dried in an oven at 100°C for 8 h ready for further derivatization and application.

Scanning electron microscopy (SEM) images have revealed that the CNSL-MTS particles are roughly spherical. The infrared spectra confirmed the successful functionalization of CNSL-MTS material with organic groups. For example, for amino functionalized samples, the peak at 1631 cm^{-1} which corresponds to the N—H bending implies successful functionalization with amino group. Nitrogen physisorption studies have further revealed that CNSL-MTS have large pore sizes of up to 25 nm, with surface area ranging from 100 to 214 m^2/g [15]. The recorded pore size of CNSL-MTS is by far larger than that of MTS materials synthesized using other neutral surfactants such as Igepal CA-720 (2.5–3.8 nm), Tergitol 15-S-12 (2.5–4.5), and Triton-X100 (2.0–60 nm) [16]. The pore size of CNSL-MTS is also larger than that of MTS prepared using nonionic block copolymer template (10 nm) [17], cationic surfactant (2.6–2.8 nm) [18], and also using a mixture of cationic and non-ionic surfactants (2.2–2.68 nm) [19]. However, the recorded surface area of CNSL-MTS (100–214 m^2/g) is smaller compared to those prepared using other neutral surfactants: Igepal CA-720 (up to 1400 m^2/g), Tergitol 15-S-12 (up to 1600 m^2/g), Triton-X100 (up to 1400 m^2/g). It is also less than that of MTS prepared using nonionic block copolymer (770 m^2/g) [17], cationic surfactant (up to 1000 m^2/g) [18], and also using a mixture of cationic and non-ionic surfactants (1432 m^2/g) [19].

2.1 Applications of CNSL templated mesoporous silica materials

The pore size of the CNSL-MTS is large enough to immobilize large molecules such as invertase enzymes. They are also suitable for removal of heavy metals from aqueous solutions and for preparation of heterogeneous catalysts such as copper(II) Schiff base catalysts.

2.1.1 Immobilization of invertase enzymes on CNSL-MTS

Enzyme immobilization can be archived via several reported methods such as covalent attachment to the surface of water-insoluble material, entrapment inside a matrix or gel that is permeable to an enzyme, substrate and products, encapsulation and adsorption of an enzyme on a solid support [20, 21]. However, there is no single immobilization method which serves well for all enzymes. The activity of the immobilized enzymes depends on the immobilization technique used, conditions required for enzymatic treatment and the characteristics of the supporting materials. The type of immobilization method chosen determines the kind of modification that must be done on the surface of supporting material before immobilizing an enzyme.

Successful immobilization of invertase enzymes on CNSL-MTS via covalent attachment has been achieved [17]. CNSL-MTS material for covalent attachment of invertase enzyme is prepared by co-condensation of tetraethoxysilane (TEOS) and

3-aminopropyltrimethoxysilane (AMPTS) using cashew nut shell liquid (CNSL) template. The resulting materials are further modified by reacting them with glutaraldehyde resulting in Glu-MTS (**Figure 3**). Activation of CNSL-MTS with glutaraldehyde offers three different kinds of interactions with an enzyme: hydrophobic, anionic exchange and covalent [22].

Immobilization of invertase on Glu-MTS by covalent method is done by stirring invertase enzyme and supported glutaraldehyde (in a 1:1 ratio) in sodium acetate buffer (pH 4.7) for 5 h at room temperature followed by overnight incubation at 4°C (**Figure 4**).

The activity of free and CNSL-MTS immobilized invertase have been tested on hydrolysis reaction of sucrose (**Figure 5**) at different temperatures, pH and substrate concentrations [5].

Initially the activities both free and CNSL-MTS immobilized invertase enzymes increase with increasing temperature and both biocatalysts show a maximum activity at 40°C. The immobilized invertase maintains stability up to 45°C, whereas the free invertase declines sharply in activity with increase in temperature above 40°C. Thus, immobilization of invertase on CNSL-MTS slightly improves thermal stability of the biocatalyst. The optimum pH for free and CNSL-MTS immobilized invertase are 5.0 and 4.0 respectively. Under these optimum conditions of temperature and pH, the activities of free and immobilized enzymes are 15,229 U and 14,833 U respectively. This corresponds to reduction of approximately 3% (upon immobilization on CNSL-MTS) of the maximal activity of the free enzyme. This indicates that no significant loss in activity occurred during the process of attaching the enzyme by covalent binding to CNSL-MTS. Similar observation have been made in activities of invertase enzymes immobilized on mesoporous materials prepared using 1,3,5-trimethylbenze (TMB) and Pluronic P123 surfactants [23].
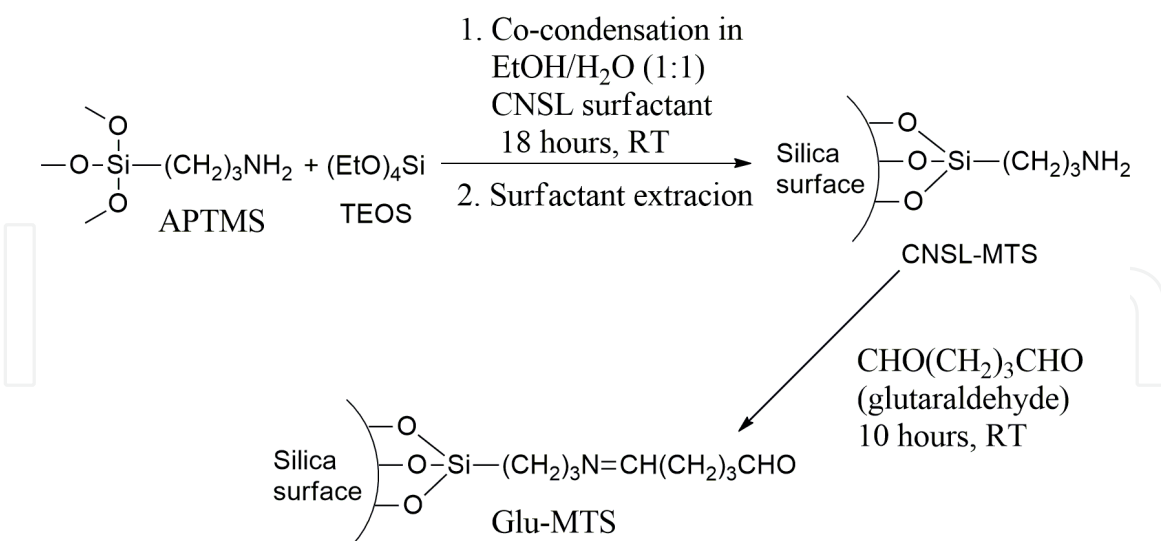

Figure 3.
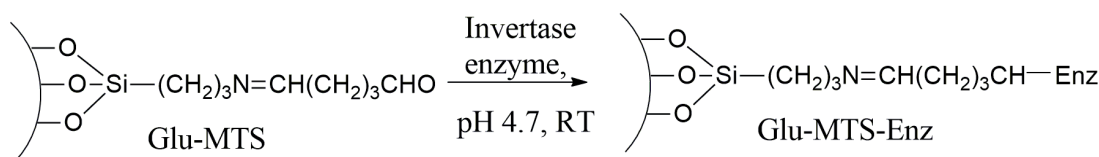*Functionalization of CNSL-MTS with glutaraldehyde.*

Figure 4.
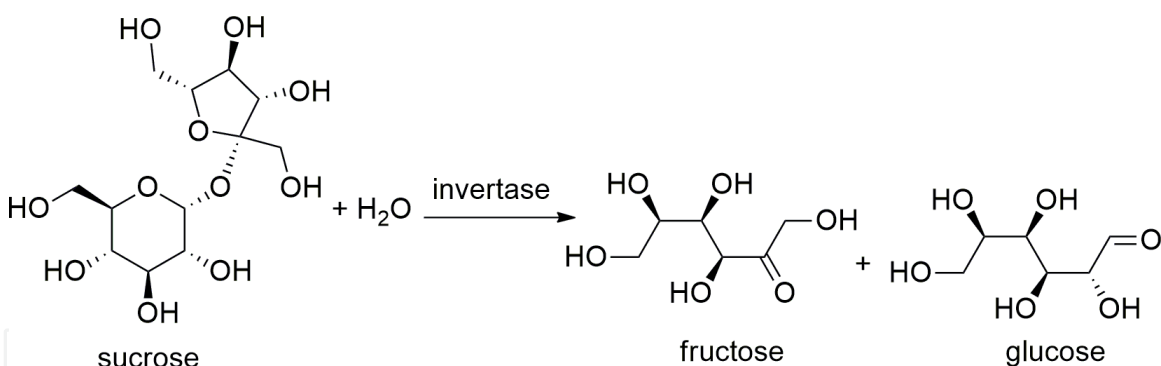*Covalent binding of the invertase enzyme onto Glu-MTS.*

Figure 5.
Hydrolysis reaction of sucrose.

The activity of CNSL-MTS immobilized invertase is higher compared to the activity of invertase immobilized on MTS material prepared using a commercially available dodecylmine surfactant (DDA-MTS); (4750U, corresponding to reduction of approximately 70% of the maximal activity of the free invertase) under the same conditions of temperature and pH.

The reuse studies of the CNSL-MTS immobilized invertase enzyme done at 40°C and pH 4.7 at five-day intervals over a range of 30 days (used for up to 10 cycles in a day) revealed that the immobilized enzyme is highly stable and can remain active when stored for over 20 days. Therefore, although the activities of CNSL-MTS immobilized invertase enzyme seems slightly lower than of free invertase, immobilized invertase is capable of being reused for up to 10 cycles in a day without significant loss of activity making the overall activity of the immobilized invertase higher than that of free invertase. Comparing the reusability of CNSL-MTS (pore size is 25 nm) and DDA-MTS (pore size is 3 nm) immobilized invertase, it has been observed that DDA-MTS based invertase maintains its activities upon reuse whereas CNSL-MTS decreases in activity. This indicates that in DDA-MTS, the enzyme is attached on the outer surface whereas in CNSL-MTS the enzyme is immobilized inside the pores. This leads to pore blockage upon reuse which reduces the access of substrate to the active sites, consequently decreasing activity. The blockage of pores after reuse leads to a drop of surface area of a catalyst from 284 m^2/g before use to 84 m^2/g after use. Similar observations have been made elsewhere in non-enzymatic heterogeneous catalysis [24].

2.1.2 Immobilization of copper(II) Schiff base catalyst on CNSL-MTS

Preparation of CNSL-MTS material for immobilization of copper(II) Schiff base catalyst involves co-condensation of tetraethoxysilane and 3-aminopropyltriethoxysilane in the stirred mixture of CNSL (template source) and aqueous ethanol (solvent) at room temperature. The resulting aminopropyl-functionalized CNSL-MTS material (MTS-AMP) is then condensed with 2-hydroxybenzaldehyde to produce the corresponding Schiff bases. Finally, the MTS supported copper(II) catalyst is obtained by the reaction of the modified Schiff base support with a solution of copper(II) acetate in water, methanol or toluene (**Figure 6**) [25].

Characterizations by nitrogen physisorption and scanning electron microscopy (SEM) have revealed that the CNSL-MTS based heterogeneous catalysts are porous with pore diameters of up to 25 nm and grain sizes of up to 1.0 mm. The maximum copper loading of CNSL-MTS based heterogeneous catalysts is about 3% w/w which is higher when compared to heterogenous catalysts prepared using commercially available dodecylamine and hexadecylamine templates (2% w/w).

The activities and reusability of CNSL-MTS supported copper(II) Schiff base catalysts have been tested on the wet oxidation of maleic acid at room temperature using H_2O_2 as an oxidant [20]. Supported copper catalysts show high activity on various
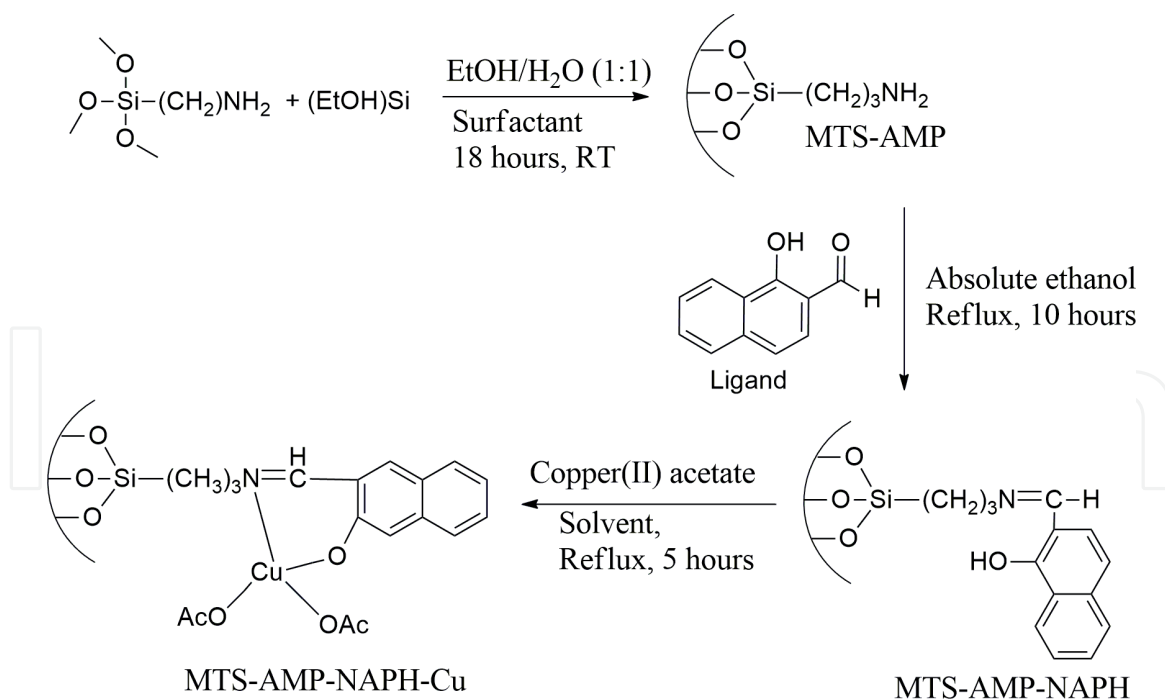
Figure 6.
Synthesis of MTS-AMP-NAPH-Cu catalyst.

oxidation reactions. For example, covalently supported copper-Schiff base complex of salicylaldehyde display an excellent catalytic activity in epoxidation reactions of various olefinic compounds using t-BuOOH as an oxidant [26]. Higher activity is also observed in wet oxidation of phenol using copper metal catalyst impregnated on MCM-41 [27].

Wet oxidation reaction of maleic acid produces carbon dioxide and water and its progress is monitored by using an HPLC technique. Although the reaction proceeds to some extent without a catalyst, it is highly accelerated by the copper catalyst. Catalysis by CNSL-MTS supported copper(II) Schiff base lead to conversion of about 95% yield after 40 min (with turn over number of about 1000) compared to less than 5% yield without catalyst after the same reaction time. Similar high activity is observed in decomposition of hydrogen peroxide (98% conversion after 50 min) using copper(II) Schiff base catalyst immobilized on SBA-15 supports (pore size = 8.8 nm, surface area = 346 m^2/g) [28]. Similar higher activity has also been reported in oxidation of sulfides to sulfoxides using H$_2$O$_2$ catalyzed by copper(II) Schiff base complex containing MCM-41 (up to 98% conversion) [29]. The interesting findings on these reported findings are not only the higher activity of the heterogeneous catalysts, but also their ability to be reused for up to five cycles without significant loss of activity.

2.1.3 Removal of lead(II) ions from aqueous solutions using CNSL-MTS

CNSL-MTS materials are modified with thiol functionality to suit lead metal ion adsorption. One way to synthesize thiol modified CNSL-MTS material is via a co-condensation of TEOS and (3-mercaptopropyl)-trimethoxysilane (MPTMS) using CNSL template. A typical synthesis involves adding TEOS and MPTMS (in 1:4, or 1:9) separately but simultaneously to a stirred solution of aqueous of ethanol and CNSL. The reaction is allowed to proceed for 18 h to obtain a thick solution which is filtered and air dried for 24 h. Finally, the template is removed by Soxhlet extraction using ethanol solvent.

Lead(II) adsorption isotherms are obtained by equilibrating CNSL-MTS samples with aqueous solution of Pb(NO$_3$)$_2$ at different metal concentrations, while maintaining a pH = 4 which is below the precipitation level of lead (pH > 6.5). After equilibration, the sample is filtered and the Pb(II) ion concentration is measured

using atomic absorption spectrophotometer. The maximum adsorption capacity observed for CNSL-MTS is 66.7 mg Pb(II) per g adsorbent. Higher adsorption of Pb(II) ions (272 mg Pb(II) per g adsorbent) using mesoporous materials with P-Containing pendant groups is reported elsewhere [30].

2.2 Synthesis of organoamine-silica hybrids using CNSL components as templates

Cashew nut shell liquid has four major components as described in the introduction section of this chapter. Investigation on which of the major component of CNSL is responsible for formation of CNSL-MTS has been done [31]. The findings show that, of the major components of CNSL cardanol is the efficient template source yielding 66% mesoporous organoamine-silica compared to anacardic acid (6%). Cardanol templated organoamine silica materials show high activity when tested with Henry reaction (as a model base catalyzed reaction) giving 81–98% yield.

3. Castor oil templated mesoporous silica materials (CO-MTS)

The preparation procedure of castor oil templated silica (CO-MTS) is more or less similar to that used in preparation of CNSL-MTS discussed in Section 2. It involves condensing a silica source such as TEOS in a stirred mixture of castor oil (surfactant) and aqueous ethanol (solvent) in acidic (HCl) medium. The reaction is allowed to proceed for 18 h. The resulting product mixture is filtered to remain with the solid which is subjected to Soxhlet extraction using ethanol as extracting solvent to give mesoporous silica (CO-MTS). Nitrogen physisorption studies have revealed that castor oil templated MTS contains: 6.7 nm pore diameter, 899 m^2/g surface area and 1.1 cm^3/g total pore volume [32]. They exhibit type IV adsorption-desorption isotherms which is characteristic of mesoporous structures. SEM analysis have reveled clusters of spherical shaped materials which suggest that growth of silica occurs within colloidal dispersions [33].

3.1 Applications of castor oil templated silica

The pore size of CO-MTS is small when compared to that of CNSL-MTS (pore diameter = 25 nm), however, they are large enough for such applications as catalysis, metal adsorptions, and immobilization of biomolecules [34, 35].

3.1.1 Amine functionalization of CO-MTS for the transesterification of tributyrin with methanol

One of the unique features of mesoporous silica material is that they provide a room for surface modification to suit a particular application. CO-MTS materials modified with Amino groups are potential base catalysts used in esterification reactions [36, 37]. Preparation of amine modified CO-MTS has been achieved via grafting method [33]. It involves dispersing the oven dried samples of CO-MTS in dried toluene followed by addition of amines such as RNH_2, NN, or DN. The resulting amine functionalized CO-MTS are termed in this case as NH_2-MTS, NN-MTS and DN-MTS respectively (**Figure 7**). Surface analysis by XPS of the chemical composition on the silica grafted groups has revealed successful attachment of N containing groups for all samples. The surface area of the CO-MTS decreases from 899 m^2/g to 510,407 and 246 m^2/g upon modification with RNH_2, NN, and DN, respectively. This indicates more significant blockage as the bulkiness of the organoamines increases [29].
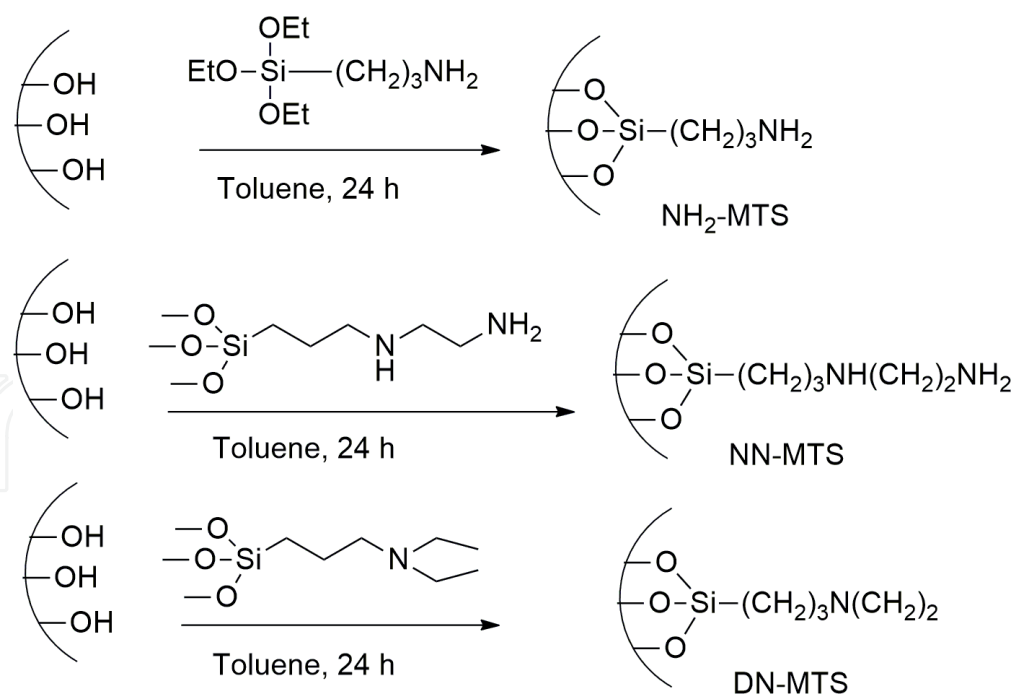
Figure 7.
Grafting amines to the MTS.

The activity of amine functionalized CO-MTS investigated on transesterification of tributyrin at 60°C showed to follow the following conversion trend: NH_2-MTS (8.9%) < NN-MTS (22%) < DN-MTS (26.7%). The trend suggests that there is an impact of amine functionality on transesterification activity and shows the superior performance of the tertiary amine. The catalysts have turnover frequencies of 0.9, 6.75 and 1.45 h^{-1} for NH_2-MTS, NN-MTS and DN-MTS catalysts respectively. The yields are relatively low compared to some reported esterification reaction (yields of above 40%) using other amine-functionalized ordered mesoporous silica, however different esterification substrates were used [38, 39].

3.1.2 Immobilization of trypsin enzymes on CO-MTS via thiol-disulfide interchange

Immobilization of trypsin on CO-MTS can be achieved via adsorption (modification is not needed) or via covalent attachment (modification is required). Immobilization of trypsin on CO-MTS has been achieved via thiol-disulfide interchange (covalent attachment). Thiol modified CO-MTS is prepared by co-condensation of 3-mercaptopropyltriethoxysilane and tetraethylorthosilicate in a 1:4 molar ratio respectively using castor oil template. Nitrogen physisorption studies have revealed that, the pore volume of thiol modified CO-MTS materials decreases from 1.0336 cm^3/g before immobilization to 0.8169 cm^3/g after trypsin immobilization [32]. The decrease in pore volume after enzyme immobilization is not strange and is due to coating of the support surface by the enzyme molecule [40].

The activity of both free and immobilized trypsin is tested on hydrolysis of N-α-benzoyl-D,L-arginine-p-nitroanilide (BAPNA). Hydrolysis of BAPNA by trypsin (**Figure 8**) cleaves the bond between the arginine and the p-nitroaniline to produce free p-nitroaniline, which is yellow and easily measured in a UV-VIS spectrophotometer.

Both free and immobilized trypsin show maximum activity on BAPNA hydrolysis at a temperature range of 35–38°C. CO-MTS immobilized trypsin show some stability up to 45°C while free trypsin has a sharp decrease on activity at that temperature. The V_{max} for free and CO-MTS immobilized trypsin are 0.32, and 0.182 U, respectively.
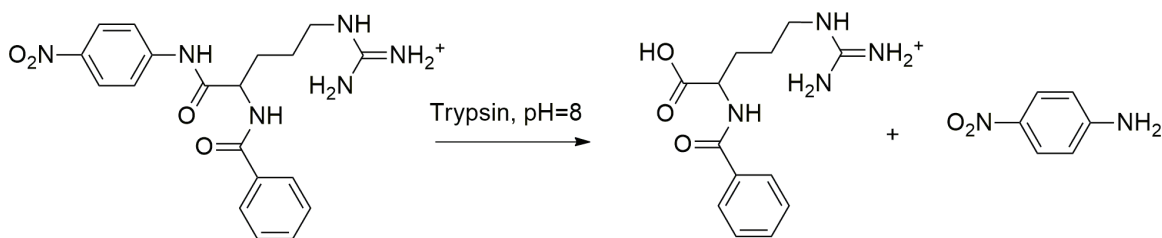
Figure 8.
Hydrolysis of BAPNA substrate for enzymatic activity assay of trypsin.

The values are not far from those reported elsewhere [35]. The immobilized trypsin is capable of being reused up to four cycles with slight decrease on its activity [32].

3.1.3 Immobilization of palladium catalysts onto CO-MTS

The CO-MTS material for immobilization of palladium catalyst is firstly modified with amino groups via the co-condensation reaction of tetraethyl orthosilicate (TEOS) and 3-aminopropyltriethoxysilane (AMPS). The reaction is carried out in ethanol/ water solvent using castor oil surfactants at room temperature. The prepared aminopropyl functionalized CO-MTS is further modified by reacting with quinoline-2-carboxaldehyde to obtain CO-MTS supported Schiff base. Immobilization of palladium catalyst is achieved by reacting the modified Schiff base support (MTS-AMP-Q), with palladium (II) chloride solution in toluene (**Figure 9**) [41].

The CO-MTS supported catalysts have been tested for activity in the wet oxidation of a mixture of phenol, ocresol and resorcinol using hydrogen peroxide oxidant. The conversion rate of the tested phenols follows the trend: resorcinol > phenol > o-cresol. The catalysts are active from room temperature to 70°C, but are slightly more effective when the reaction temperature is greater than room temperature. For instance, in 60 min of reaction, the catalyst achieves about 50% of phenolic degradation at room temperature and about 55% conversion at 70°C. Other reports have shown even better phenol conversion of up to 100% [42–44].
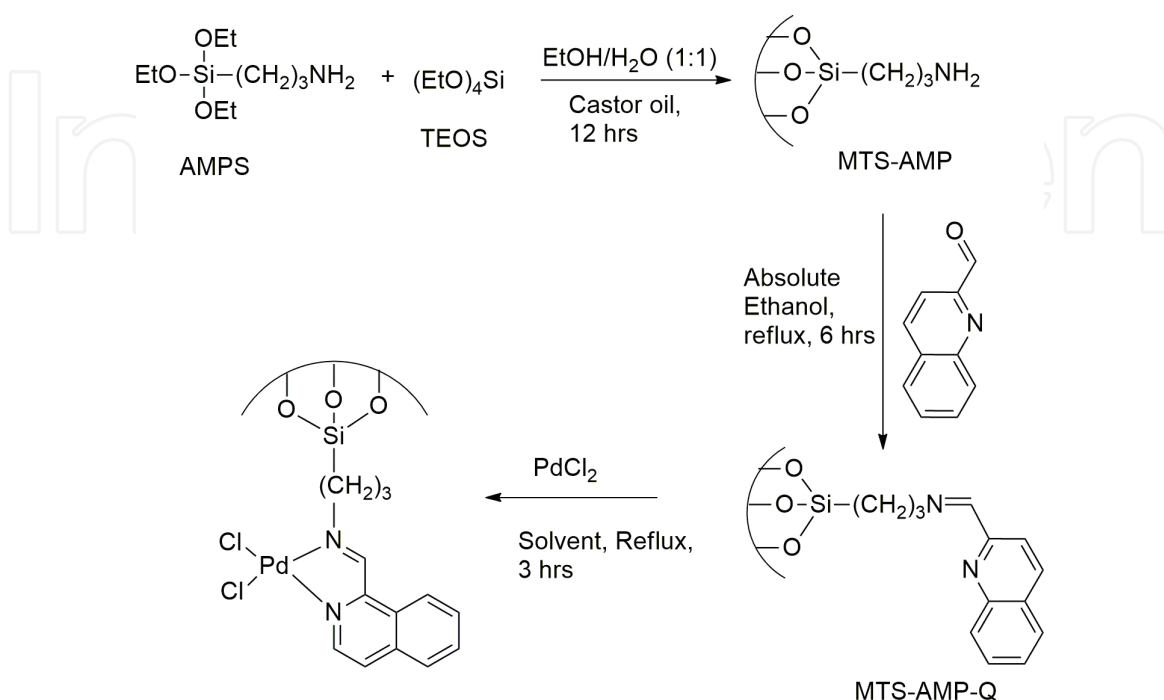

Figure 9.
Stepwise preparation of CO-MTS supported palladium catalyst.

4. Sunflower oil templated mesoporous silica (SO-MTS)

Sunflower oil has also been reported to be a potential renewable surfactant for synthesis of mesoporous materials. However, sunflower is an edible oil and therefore its use as raw material in industries is highly likely to face competition from food production. Mesoporous materials prepared using sunflower oil have pore diameter of up to 10.1 nm with surface area of 734.1 m^2/g [45].

4.1 Adsorption studies of Cr(III) using cyano functionalized SO-MTS

Preparation of cyano functionalized SO-MTS materials is achieved by one pot co-condensation of 2-cyanoethyltriethoxysilane (CETS) and tetraethoxysilane (TEOS) using sunflower oil as templating agent. The adsorption sites are either the tethered cyano groups or carboxylic groups obtained by hydrolysis of cyano groups (**Figure 10**).

The functionalized SO-MTS materials have adsorption maximum of 19.7 mg Cr(III) ions per g of adsorbent. Adsorption studies of Cr(III) ions from tannery wastewater have revealed that functionalized SO-MTS material can remove Cr(III) ions up to 83% [27].
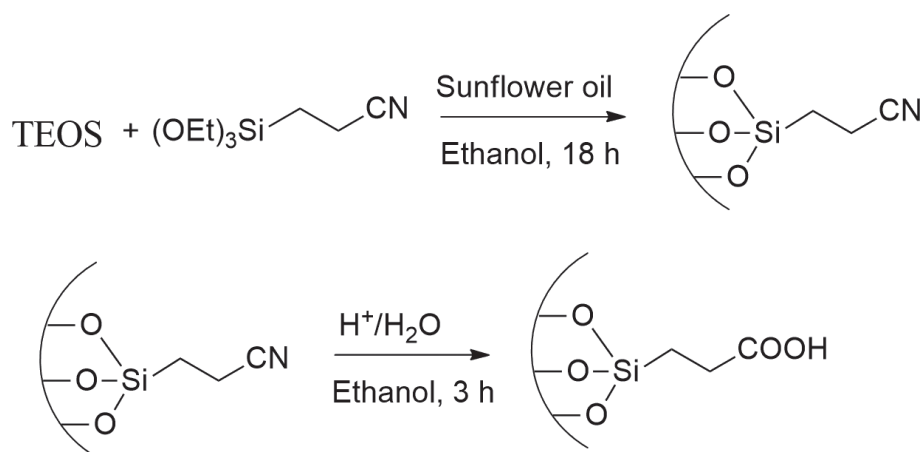

Figure 10.
Synthesis of sunflower oil templated MTS-CN and MTS-COOH.

5. Conclusion

Details of routes to synthesis of mesoporous silica materials using renewable surfactants as potential sources of templates are well covered. Cashew nut shell liquid, castor oil and sunflower oil have all shown to be good bio-based sources of templates for synthesis of mesoporous silica materials. The prepared materials using these bio-based surfactants have surface properties desirable for potential applications such as enzyme immobilization, preparation of heterogenous copper(II) Schiff base catalysts and removal of heavy metals by adsorption. Heterogenous catalysts prepared using these bio-based surfactants have shown high activities, reusability, and stability. Heavy metal removal by adsorption of up to 80% has been archived.

Conflict of interest

There are no conflicts of interest.

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