Synthesis and characterization of mesoporous silica nanoparticles using ionic liquids as a template

N Rameli, K Jumbri, R A Wahab, A Ramli, F Huyop

Abstract. Mesoporous silica nanoparticles (MSN) were successfully synthesized using different types of ionic liquids (ILs) with different length of side alkyl chain as the template. The formed MSN were characterised by FTIR, XRD and BET. In this study, ILs of long alkyl chains of cation was found to decrease the pore size of the MSNs thus, increasing the surface area. FTIR spectroscopy affirmed the formation of SiO while the broad peak in the X-ray diffractogram conveyed that the silica of MSNs is amorphous.

1. Introduction

Mesoporous materials are classified under porous material based on their pore diameter. Consequently, the three types of pores can be categorized into micro-, meso-, and macroporous. The pore diameters of mesoporous materials are characteristically ranged between 2 to 50 nm [1]. These materials are typically prepared by formation of silica around template micelle assemblies followed by template removal by calcination. The applicability of mesoporous materials has since been extended as carriers for drug delivery due to their unique pore size, high surface area and pore volume. Pore size of the mesoporous material for such application is tunable using different types of templates and by changing the reaction parameters [2].

Mesoporous silica nanoparticles (MSN) are ordered mesoporous materials based on silicates obtained by sol-gel and hydrothermal synthesis to result in stable and enlarged mesopores. MSNs are known for great properties such as pores with well-defined sizes and uniform shapes. Moreover, pore size of MSNs can be modulated by changing the length of the template molecule. A new mesoporous system may also be fabricated by changing the silica sources, surfactants, or reaction conditions viz. temperature, aging time, mole ratio of reactants and pH of the medium.

Silica precursors i.e. tetraethyl orthosilicate (TEOS) are insoluble in water, hence usually require the addition of ethanol as a homogenizing agent in the reaction. To solve this issue, a new silica precursor, tetraakis(2-hydroxyethyl) orthosilicate (THEOS) that has a water-soluble residue i.e. ethylene glycol, was introduced [3]. THEOS when dissolved in water is hydrolysed into glycol and silicic acid, which then condenses into silica. Utilization of THEOS offers the advantage of an eco-friendly process to fabricate structured silica, since the formed silica is easily hydrolysed and polymerised at neutral pH condition, and can undergo jellification at ambient temperature [4]. Moreover, silica formation using THEOS as the precursor only liberates glycol instead of alcohols, hence is more biocompatible [4-6].
The widely used surfactant-template method to synthesise MSN was originally founded by scientists at Exxon Mobil in 1992 [6]. Surfactants are the typical templates for synthesising MSN, as these compounds are capable of forming micelles. In this reaction, the silica source would aggregate and form silica networks around the micelles. Till recently, ionic liquids (ILs), composed of organic salts were used as alternative templates to prepare MSN, following their reported versatility, for instance, good solubility and amphiphilic properties. The salt effect of ILs are due to the unique architecture of the inorganic anion and organic cation [7]. Interestingly, ILs can electrostatically interact with silicates to form mesopores structures. Although short chain ILs are less capable of forming micelles, these unique compounds may still form MSNs, even ones showing random porosity [8].

Li et al. investigated the effect of amphiphilic room temperature ionic liquid (RTILs) using different alkyl chain lengths. It was discovered that longer alkyl chain lengths ILs tend to form MSNs with bigger pores [9]. This has somewhat to do with an additional π-π stacking association between the imidazolium cation and long alkyl chain on the cation of IL, which led to the enlargement of pores in MSNs. Likewise, Zhang et al. [10], examined the effect of several anions (BF$_4^-$, NTf$_2^-$, CFSO$_3^-$) and cations of IL of MSN formation. It was shown that the alkyl chain length on imidazolium cation and IL concentration in the reaction system significantly impacted the pore structure and thermal stability of the silica gel materials. Mesoporous silicas with 1-alkyl-3-methylimidazolium tetrafluoroborate as the template produced larger pore sizes but yielded lower surface area. This is the consequence of the strength of hydrogen bonds between the water molecules and anions, in the order of BF$_4^-<$ NTf$_2^-<$ CFSO$_3^-$ [11].

Rapid development of mesoporous materials in fields like catalysis, separation, ion exchange, molecular sieving and adsorption is directly due to their comparable potential to zeolites. However, further applications of MSNs are still limited, mainly because of the inability to properly control the pore size and particle size as well as their morphology. Therefore, the present work is aimed in synthesising and characterising the MSN. The effect of different types of ILs based on length of side along the pore and particle size, as well as the surface area of MSN is also investigated.

2. Materials and method

2.1 Materials

Tetrakis (2-hydroxyethyl) orthosilicate (THEOS) was obtained from Gelest. Ionic liquids (ILs), 1-butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl) imide [bmim][NTf$_2$] were purchased from Sigma-Aldrich while hexadecyltrimethylammonium bromide (CTAB) were synthesised in lab.

2.2 Synthesis of mesoporous silica nanoparticles

The IL (1 mL) was dissolved in 70 mL distilled water followed by dropwise addition of 5 mL of THEOS and the mixture was stirred at 60°C for 1 h. The sample was then transferred into a hydrothermal vessel and heated at 90°C for 24 h. The solid product was filtered, washed with ethanol to remove ethylene glycol, filtered again and dried at 80 °C for 24 h. Finally, the product was calcined at 550°C for 4 h. The same procedure was repeated using different ILs to prepare of types of MSN. For clarity, MSN prepared from different ILs were designated as MSN-C(CTAB) and MSN-T ([bmim][NTf$_2$]) as Figure 1 show the molecular structure.

Hexadecyltrimethylammonium bromide (CTAB)

1-butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl) imide ([bmim][NTf$_2$])
Figure 1: Molecular structures of hexadecyltrimethylammonium bromide (CTAB) and 1-butyl-3-methylimidazoliumbis(trifluoromethylsulfonyl) imide ([bmim][NTf$_2$])

2.3 Characterization
The composition and pore structures of the formed MSNs were characterized by the following spectroscopic and microscopic methods, FTIR, XRD and BET. The materials were characterised for their textural properties and surface details. Fourier transform infrared spectroscopic (FTIR) analysis was performed on a Thermo Scientific Nicolet while the structural properties of the MSNs were obtained using a low angle powder X-ray Diffraction (XRD, Bruker AXS D8). Textural properties of the MSN samples were analysed by nitrogen physisorption analysis using Micromeritics ASAP 2020 setup. Prior to each analysis, calcined MSN samples were degassed for 2h at 250°C at ramping of 10 °C/min for 4h under vacuum to remove all physisorbed species from the surface of the sorbent in the degas port of the apparatus. N$_2$ adsorption/desorption analysis was performed to examine the porosity and surface area of the MSNs.

3. Results and discussion
3.1 FTIR analysis
Mesoporous silica nanoparticles were synthesized for about 3 days synthesis duration. FTIR of uncalcined and calcined of MSN were compared to characterise the component of the MSN. For the uncalcined MSN (MSN-T), presence of a silanol (Si-OH) peak at 956 cm$^{-1}$ was indicative of physisorbed water molecule. The finding is consistent with an earlier work by Handke & Hwasny [12]. They reported that the peak assigned to the Si-OH group was only observable in the spectrum of silica, as the result of the preparation method and hygroscopic properties. Upon calcination (MSN-C), the spectrum of MSN showed a marked increase of Si-OH peaks and all the MSN samples show peaks that were characteristic for SiO$_2$ only (Figure 2). This infers that the volatile component was completely removed from MSN by calcination [13]. The spectra of MSN-T exhibited a peak between 1054.65–1069.88 cm$^{-1}$. This was attributed to the asymmetric vibration of Si-O-Si bond. A peak that emerged between 801.37–806.37 cm$^{-1}$ was due to the symmetric stretching vibration of Si-O-Si (MSN-T) [14] [15]. The intensity of the absorption peak of SiO$_2$ was increased hence, indicating that the MSN was successfully formed and most of the templates used in the fabrication process were removed [16].

Figure 2: FTIR spectra of MSN of uncalcined and calcined MSN-C and MSN-T
of micelles participation were the hysteresis loop. The almost negligible absorption branch of the isotherm. The mesopore size for MSN type H2 hysteresis. Therefore, the pore phenomenon is usually due to constrictions of disordered and adsorption branch and a steep desorption branch in the mesopores hysteresis loop. An isotherm indicates that mesoporous materials classification, the presented isotherms for all samples are of type IV, hence characteristic of mesoporous materials. This isotherm exhibits a maximum range relative pressure P/P0 = 0.6–1.0 which indicates that the formed MSN possessed large size mesopores [16], as inferred from the presence of a hysteresis loop. An isotherm that has a hysteresis loop is the result of capillary condensation of N2 gas in the mesopores.

MSN-T and MSN-C exhibited H2 type hysteresis loop, characterized by a smooth increase adsorption branch and a steep desorption branch. A H2 type loop often indicates that the materials are disordered and have not well-defined pore size and shape. The isotherm also has an ink-bottleneck constricted shape pores (Figure 3: A and B), which likely means the occurrence of pore blocking. This phenomenon is usually due to pore constriction during evaporation of the capillary condensate [20]. Therefore, the pore liquid evaporates at a given pressure leading to a step desorption, distinctive of a type H2 hysteresis.

Figure 5 shows a broad distribution of pore size in the range of 5.0–18.0 nm for both MSN-C and MSN-T, belonging to mesopore category. The pore size distribution was calculated using BJH analysis from adsorption branch of the isotherm. The mesopore size for both materials was found almost negligible, suggesting MSNs with irregular pores were formed, as supported by the shape of the hysteresis loop. The data indicate that the formed inconsequential mesopores of different sizes were the result of intrusions by ILs. Formation of variable pore sizes could be explained by the miscibility of ILs [15]. Moreover, the steric hindrance of the cation might have caused incomplete participation of the ILs in the micelle formation, that consequently led to formation of unequal values of micelles.

Figure 3: XRD of MSN with different of IL used as template

3.2 Solid state characterization by XRD
The X-ray diffractograms of the different MSNs are shown in Figure 3. A broad peak at range 2θ = 20°-25° were obtained for MSN-T and MSN-C. The data revealed that the MSNs were amorphous. Conversely, Zhang et al. [10] had indicated that XRD characterisations was not always affirmative of the formation of crystallised silica. This shows that the formed silica materials was amorphous [17]. The reason for the absence of an intense signal in these XRD pattern might be due to the lack of large diffraction domains, consistent with the fact that MSNs are of small nanoparticles size [18]. In case for MSN-T which used 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([bmim][NTf2]) as the template, the XRD spectrum showed a visible peak at 2θ = 2.3°, although its intensity is low. These visible peaks of MSN-T that indicated the sample might have a certain degree of structural ordering [15], [19].

3.3 Porous properties
Figure 4 illustrates the N. adsorption/desorption isotherm for SiO2 samples. Based on the IUPAC classification, the presented isotherms for all samples are of type IV, hence characteristic of mesoporous materials. This isotherm exhibits a maximum range relative pressure P/P0 = 0.6–1.0 which indicates that the formed MSN possessed large size mesopores [16], as inferred from the presence of a hysteresis loop. An isotherm that has a hysteresis loop is the result of capillary condensation of N2 gas in the mesopores.
The template acts as surfactant played important roles in the formation of mesoporous materials. As shown in Table 1, all MSNs with varied templates content were characterised to be mesoporous having different pore sizes and BET surface areas. It is shown that the pore size of the silica decreases considerably as the alkyl chain length was increased. This observation is due to the critical micelle concentration (CMC) of the template. When the length of alkyl chain increase, CMC of template decreased that easier the micellization. The steric hindrance of the long alkyl chain cause the formation of micelles become more entangled and closed packed. Thus, the pore size become smaller.

Figure 4: N$_2$ adsorption/desorption of MSN-C and MSN-T. A) Ink-bottleneck pore network of H$_2$.

Figure 5: Pore size distribution of MSN-C and MSN-T.
The study found that different anions resulted in the remarkably different pore sizes and surface areas of MSNs. The increase in size of the anion leads to the template formed to the surface faster and makes more strict environment for micelle formation. By selecting IL templates with different cation and anion, different kinds of pore structure can be formed.

**Table 1**: Textural properties of MSN with different IL.

| Sample | BET surface area (m/g) | Pore volume (cm/g) | Pore size (nm) |
|--------|------------------------|--------------------|----------------|
| MSN-C  | 635                    | 0.90               | 5.83           |
| MSN-T  | 572                    | 1.20               | 7.56           |

### 4. Conclusion

In the present study, we explored a way to synthesis silica mesopores using ILs as a template. MSNs were successfully produced by hydrothermal method with THEOS as precursor and ILs as the template. Different types of IL cations and anions would exert varying effects on the pore size, surface area and even the particle size of the amorphous MSNs. Using IL in the synthesis of MSN samples gave wide a hysteresis loop in the N sorption, suggestive of formation of mesopores. Other than that, ILs formed micelles with irregular mesoporous structures which is proven by the broad pore size distribution. The findings in this study would, therefore, pave a way of using ILs to further explore synthesis of novel MSNs and to expand their applications into other fields.

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