Jurnal
Teknologi

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# Synthesis of Nanosiliceous Zeolite and its Functionalization with Silane Derivatives

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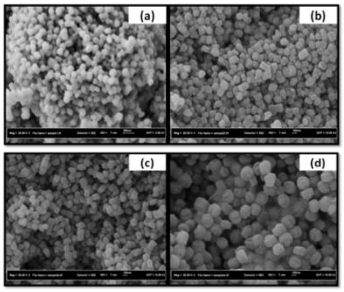
**Article history**

Received :18 March 2013
Received in revised form :
26 April 2013
Accepted :17 May 2013

**Graphical abstract**



## Abstract

A nanosiliceous zeolite has been synthesized using hydrothermal method. Theoretically, nanosiliceous zeolite contains a lot of silanol group which allow the functionalization process for surface modification. Siliceous zeolite of the type silicalite (Sil) has been synthesized hydrothermally at 150°C for 4 days. The silicalite material was then functionalized with silane derivatives i.e 3-(triethoxysilyl)-propylamine (APTES), octadecyltrichlorosilane (OTS) and (3-mercaptopropyl)-trimethoxysilane (MPTS) using post-synthesis method. XRD results showed the formation of silicalite phase crystallinity. The FTIR result showed that Sil-OTS gave the highest intensity of the vibration assigned for silane derivative, followed by Sil-APTES and Sil-MPTS. The BET surface area of the functionalized-Sil decreased, showing the attachment of silane derivatives to silicalite has occurred. FESEM results showed sheet of hexagonal stick together to form granule-like crystal morphology of functionalized-Sil samples with larger particle size was observed for Sil-OTS, followed by Sil-APTES and Sil-MPTS after functionalization process. The functionalized-Sil sample is expected to be a good support for chemosensor molecules.

*Keywords*: Siliceous zeolite; nanosilicalite; silane derivatives; functionalization

## Abstrak

Zeolit nanosilika telah disintesis menggunakan kaedah hidroterma. Secara teorinya, zeolit nanosilika mengandungi banyak kumpulan silanol yang membolehkan proses penggabungan bagi pengubahsuian permukaan. Zeolit silika jenis silikalit (Sil) telah disintesis menggunakan kaedah hidroterma pada suhu 150°C selama 4 hari. Silikalit difungsikan dengan beberapa terbitan silana iaitu 3-(trietoksisilil)-propilamina (APTES), oktadesiltriklorosilana (OTS) dan (3-merkaptopropil) trimetoksisilana (MPTS) menggunakan kaedah pos-sintesis. Keputusan XRD menunjukkan pembentukan fasa hablur silikalit. Keputusan FTIR menunjukkan yang Sil-OTS memberikan intensiti getaran tertinggi bagi getaran terbitan silana diikuti oleh Sil-APTES dan Sil-MPTS. Keputusan luas permukaan BET silikalit yang difungsikan semakin berkurang menunjukkan bahawa pergfungsian terhadap terbitan silana kepada silikalit telah berlaku. Keputusan FESEM menunjukkan morfologi hablur lapisan heksagon yang bercantum membentuk seperi butiran kristal bagi silikalit yang difungsikan, dengan saiz zarah Sil-OTS terbesar diikuti oleh Sil-APTES dan Sil-MPTS selepas proses pengfungsian. Sampel Sil-berfungsi ini dijangka menjadi penyokong yang baik bagi molekul kimosensor.

*Kata kunci:* Zeolit silika; nanosilikalit; terbitan silana; pengfungsian

## ■1.0 INTRODUCTION

Zeolites have drawn increasing attention in recent years because of their well-defined crystalline structures with uniform micropores.[1] The synthesis of nano-meter sized zeolites has received much attention due to the utility in fundamental studies of zeolite growth such as, in preparation of ultra-thin zeolite films and nano-composite, and also for catalytic and photochemical reactions.

Generally, nanosized zeolite crystals are hydrothermally synthesized under microwave irradiation.[2] The external surface area of nanoscale zeolites is up to an order of magnitude larger than the external surface area for micrometer sized zeolites and provides an additional surface area for reaction, and further functionalization. This surface functionalization of the zeolites are widely used in biomedicine and diagnosis such as, biomedical imaging,[3] and drug delivery,[4] and in the development of low dielectric materials for the semiconductor industry.[5,6]

So far three methods for the functionalization of silica were reported. Firstly, the post-modification (grafting) method, where a subsequent grafting of colloidal nanosilica was prepared by using alkoxysilane as a sol–gel precursor and aminoorgano functional alkoxysilane as a modifier. Secondly, in situ modification (co-condensation method), where simultaneous modification of silica via preparation of colloidal nanosilica using alkoxysilane and modifier. Finally, incorporation modification method, the incorporation of organic groups as bridging components directly into the pore by the use of organosilica precursors for the production of periodic organosilicas.[7] This method can be used to immobilize different types of chromophores into suitable porous nanosilica derivatives according to the type of analytes.

The focus of this work is on the synthesis and characterization of nanosiliceous zeolite of the type silicalite and its functionalization with silane derivatives. Synthesis of silicalite (purely siliceous form of ZSM-5) has been reported by several groups.[8-12] The silicalite is of interest as it has the MFI type structure and purely formed siliceous silicalite could provide surface silanol that can facilitate the functionalization with silane derivatives. The functionalization of silane agent on the surface of nanosiliceous zeolite is expected to have a good linkage to bind silica-based material with luminol for chemosensor application.

## ■2.0 EXPERIMENTAL

### 2.1 Materials and Methods

Chemicals used for the synthesis viz., tetraethyl orthosilicate (TEOS, Merck) as silica source, tetrapropylammonium hydroxide, (TPAOH, Merck, 40 wt.% in water), as template, sodium hydroxide pellet, (NaOH, Merck) as an alkaline source, and ethanol (EtOH, Merck) were purchased from the commercial sources and were used as received. For the functionalization, 3-aminopropyltriethoxysilane (APTES, Merck), 3-mercaptopropyltrimethoxysilane (MPTS, Merck) and octadecyltrichlorosilane (OTS, Merck) were used as silane derivatives to be functionalized to the nanosiliceous zeolite. Toluene was used as solvent in the functionalization method.

A Bruker D8 X-ray diffractometer with Cu Kα target was used to collect XRD powder patterns for the samples. XRD patterns were collected between 2θ angles of 5° and 50°. The crystal sizes were estimated using Scherrer's equation given in Eq. 1:

$$L = \frac{K\lambda}{B\cos\theta_B} \qquad (1)$$

where,

L = Crystallite size
$\lambda$ = wavelength of the XRD peak (1.542 Å)
$\theta_B$ = Bragg's angle
B = FWHM (full width at half max)
K = Constant which is approximately 0.9

The presence of tetrahedral $TO_4$ (T = Si or Al) bonding is determined by using Fourier Transform Infrared Spectroscopy, FTIR (Perkin Elmer series 1600). The spectrum was elucidated for zeolite framework structure at wavelength between 400-4000 $cm^{-1}$. The Brunauer–Emmett–Teller (BET) method was used to determine the surface area of obtained silicalite. The morphology of silicalite was elucidated using Field Emission Scanning Electron Microscopy, FESEM (JEOL).

### 2.2 Synthesis of Silicalite

Silicalite has been synthesized from clear gel solutions according to the general procedure of Petushkov and co-workers[6] with several modifications. Silicalite was hydrothermally synthesized using molar ratio as tabulated in Table 1. Firstly, tetraethylorthosilicate, TEOS (26.04 g, 0.12 mol) was added to the tetrapropylammonium hydroxide, TPAOH (22.88 g, 0.11 mol) with constant stirring. Sodium hydroxide (0.032 g, 8.0 x $10^{-4}$ mol) in distilled water (24.65 g) was then added to the mixture of TEOS and TPAOH solution drop wise. The mixture was stirred for 1 h in an oil bath at 60-70°C. The mixture was then transferred into stainless steel autoclave with PTFE liner and heated in an oven at 150°C for 4 days. The product obtained after heating was centrifuged for about 20 min to separate the solid product from supernatant. The obtained solid sample was washed once with ethanol (50 mL) and twice with deionized water (100 mL) followed by drying in an oven at 90°C overnight. The dried sample was then calcined at 600°C for 6 h to remove the organic template.

**Table 1** Molar ratio for the synthesis of silicalite

| Name | Molar ratio |
|---|---|
| silicalite | 25TEOS: 9TPAOH: 0.16NaOH: 495$H_2O$ |
| silicalite-EtOH | 25$SiO_2$:9TPAOH:0.16NaOH: 495$H_2O$: 100EtOH |

### 2.3 Functionalization of Calcined Silicalite

Functionalization with silane derivatives containing amine group was carried out by refluxing a mixture of silicalite (2 g) and 3-aminopropyl-triethoxysilane (APTES) (2 g, 9.05 x $10^{-3}$ mol) in toluene (60 mL) for 4 h. The solid was separated by centrifugation and washing with toluene. Functionalization with silane derivative containing thiol groups was carried out by refluxing a mixture silicalite (2 g) and 3-mercaptopropyltrimethoxysilane (MPTS) (2 g, 0.01 mol) in toluene (60 mL) for 4 h followed by centrifugation and washing of the silicalite powder with toluene. For functionalization with octadecyltrichlorosilane (OTS), silicalite (0.5 g) was immersed in toluene (5 mL) containing OTS (0.19 g, 500 µmol). Then the suspension was shaken for 5 min at room temperature. The solid was collected by centrifugation and lastly dried at 90°C for 5 h.

## ■3.0 RESULTS AND DISCUSSION

### 3.1 Synthesis and Characterization of Silicalite

X-ray powder diffraction patterns of silicalite and silicalite-EtOH is shown in Figure 1. The result showed that the synthesized samples possess crystalline structure with the peaks pattern corresponding to MFI type zeolite. Estimated crystallite sizes from Scherrer's equation for silicalite and silicalite-EtOH are 28.39 and 30.23 nm, respectively suggesting that both are in nano-meter range size. Both samples show monoclinic symmetry, evident from the appearance of doublets at peak positions, 2θ 24.56° – 25.95°, 29.41° – 29.95°, and 48.54° – 48.91° for silicalite. While for silicalite-EtOH, the doublet appeared at peak positions, 2θ 8.85° – 9.84°, 23.69° – 23.93°, and 30.00° – 30.39°, respectively.

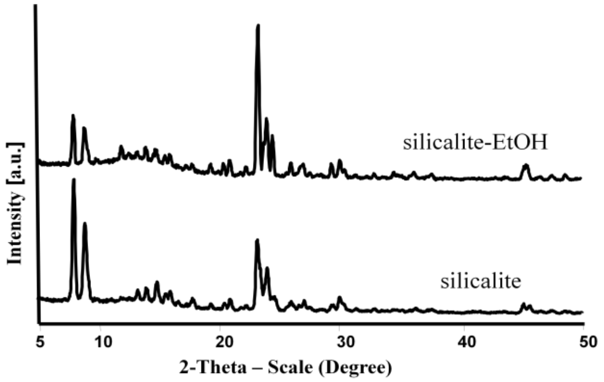


**Figure 1** X-ray powder diffraction patterns of (a) silicalite and (b) silicalite-EtOH

Figure 2 shows the FTIR spectra of silicalite and silicalite-EtOH. Intensive bands with medium intensity at around 1227 cm$^{-1}$ and 800-790 cm$^{-1}$ represent structurally sensitive asymmetric Si-O-Si stretching and symmetric Si-O-Si stretching vibrations of the silicalite framework. The presence of band at around 548 cm$^{-1}$ which corresponds to the to the double D5R ring, confirmed the formation of MFI type structure. The band observed at *ca*. 458 cm$^{-1}$ is attributed for Si-O-Si bending vibrations while an intense band at *ca*. 1100 cm$^{-1}$ is assigned for asymmetric stretching of tetrahedral SiO$_4$ are non structural sensitive. Table 2 summarizes the main IR stretching bands of silicalite samples.

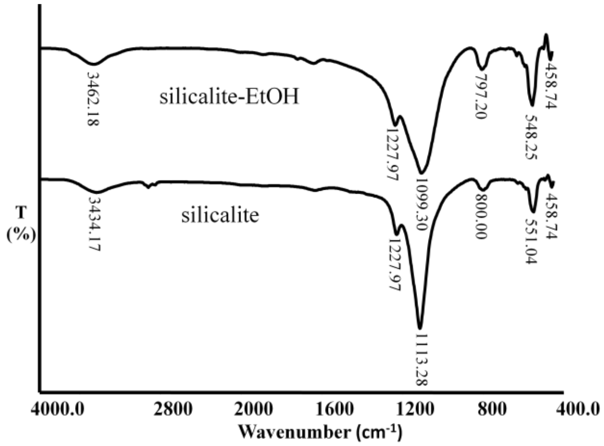


**Figure 2** FTIR spectra of silicalite and silicalite-EtOH

**Table 2** Main IR stretching bands for silicalite samples

| Peak Positions (cm$^{-1}$) | Type of vibration |
|---|---|
| 1227 | Asymmetric SiO$_4$ stretching (structure sensitive) |
| 1100 | Asymmetric SiO$_4$ stretching (non-sensitive) |
| 800-790 | Symmetric Si-O-Si stretching (structure sensitive) |
| ~548 | Double D5R ring for MFI crystal |
| 458 | Bending Si-O-Si |

## 3.2 Functionalization of Silane Derivatives to the Silicalite

The X-ray powder diffraction patterns of silicalite after functionalization process is shown in Figure 3. No significant changes of the diffractograms were observed after functionalization process, which indicated that the crystalline structure of silicalite particles was retained. The crystallite size of functionalized silicalite samples increased slightly after the functionalization process. Sil-OTS sample gave the largest size among the functionalized silicalite samples suggesting that higher numbers of OTS molecule has been functionalized on silicalite. Another reason for larger size shown by Sil-OTS sample might be due to OTS having larger molecular size as compared to APTES and MPTS silane derivatives Table 3 shows the crystallite size of the functionalized silicalite samples

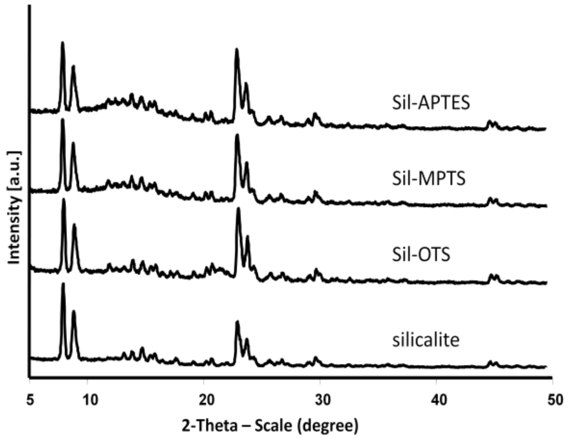


**Figure 3** X-ray powder diffraction patterns of silicalite, Sil-APTES, Sil-MPTS and Sil-OTS

**Table 3** Crystallite size of silicalite and after the functionalization

| Sample | Crystallite size (nm) |
|---|---|
| silicalite | 28.39 |
| Sil-APTES | 28.50 |
| Sil-MPTS | 29.54 |
| Sil-OTS | 30.46 |

Figure 4 shows the FESEM micrograph of silicalite and silicalite after the functionalization process. The morphology of the samples is a sheet of hexagonal stick together to form granule like crystal and the silicalite morphology does not change significantly after functionalization with silane derivatives. However, the particle size of silicalite increased after functionalization process. Table 4 shows the average particle size calculated from the FESEM results. Sil-OTS shows the largest particles compared to the Sil-APTES and Sil-MPTS with 2-fold increase in particle size as compared to silicalite. The results from FESEM is in good agreement with the results obtained from estimated size calculated from Scherrer’s equation (Table 3)

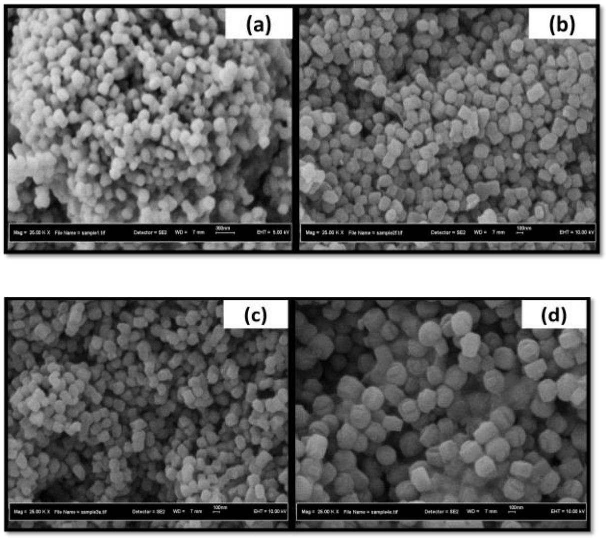


**Figure 4** FESEM micrograph of (a) silicalite, (b) Sil-APTES, (c) Sil-MPTS and (d) Sil-OTS (Magnification 25.00 K)

**Table 4** Average particle size of silicalite and after the functionalization

| Sample | Average particle size (nm) |
|---|---|
| Silicalite | 168.60 |
| Sil-APTES | 206.32 |
| Sil-MPTS | 181.30 |
| Sil-OTS | 377.70 |

The FTIR spectra of silicalite after functionalization with APTES, MPTS and OTS are illustrated in Figure 5. Based on the spectra, there are bands observed at *ca*. 2850 and 2920 cm$^{-1}$. These bands were assigned to symmetric and asymmetric stretching vibrations of C-H of the silane molecules. The spectrum of Sil-OTS showed the most intense with highest C-H band intensities, follows by Sil-APTES while C-H vibration for Sil-MPTS can hardly be observed. This observation indicated that OTS having long alkyl chains in its molecule is expected to show higher amount of C-H vibration which reflects in its higher intensities. Between Sil-APTES and Sil-MPTS, with smaller size of APTES and MPTS, it can be seen that larger amount of APTES molecules have been functionalized by silicalite as compared to Sil-MPTS, since higher intensities of the C-H bands are shown by this sample. These FTIR results of the functionalized silicalite samples support the results obtained by FESEM.

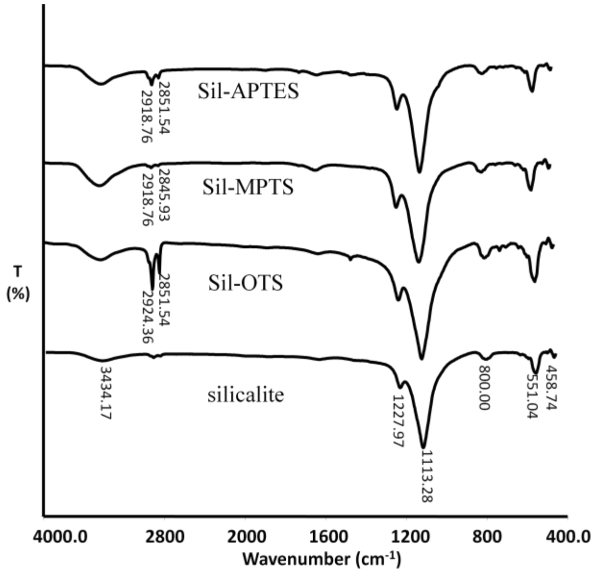


**Figure 5** FTIR spectra of silicalite, Sil-APTES, Sil-MPTS and Sil-OTS

The BET surface area was measured to monitor the change of available surface area of calcined and functionalized silicalite.The successful functionalization of silane derivatives by silicalite can also be monitored by the surface area of the sample. BET surface area of the silicalite and the functionalized silicalite is shown in Table 5.

**Table 5** BET surface area for silicalite before and after functionalization

| Sample | BET surface area (m$^2$/g) |
|---|---|
| Silicalite | 403.41 |
| Sil-APTES | 248.63 |
| Sil-MPTS | 393.24 |
| Sil-OTS | 8.29 |

As can be seen from the table, the BET surface area of all functionalized silicalite decreased as compared to silicalite. This indicated that the silane derivatives have been successfully attached to the silicalite sample. The Sil-OTS showed the lowest surface area due to the bigger size of OTS that attached on the surface of silicalite, in such a way the molecules covered the pore of silicalite. APTES was also been substantially attached to silicalite as the surface area of the Sil-APTES has decreased significantly. On the other hand no significantly change in BET surface area for Sil-MPTS which can be concluded that only very small amount of MPTS molecules have been successfully functionalized by silicalite. This is the reason why the intensities of C-H vibration of Sil-MPTS can hardly been observed in its IR spectrum (Figure 5).

## ■4.0 CONCLUSION

Nanosiliceous zeolite of the type silicalite was successfully synthesized using hydrothermal method. The characterization using XRD shows the crystallinity phase of silicalite in nanometer size. The results from FESEM, FTIR and BET surface area have shown that silane derivatives of OTS and APTES have been successfully functionalized by silicalite while MPTS was unable to attach to silicalite. In this study APTES has shown a promising functionalized agent on silicalite surface as it contains primary amine group in its molecule that can further be reacted with luminol to produce luminol functionalized silica chemosensor application.

## Acknowledgement

The authors thank Universiti Teknologi Malaysia and Malaysian Ministry of Higher Education (MOHE) for financial fundings through Geran Universiti Penyelidikan (GUP) Q.J130000.2626.06J43 and also to the National Nanotechnology Directorate (NND) fund (Q.J130000.7926. 4H007).

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