

Functionalization of Mesoporous Si-MCM-41 by Grafting with Trimethylchlorosilane

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Abstract

The production of functionalized mesoporous silicas has attracted great attention in the last years. In particular, the uses of organosilanes, as modification agents, has been largely studied due mainly to the increasing requirements deriving from the area of polymer nanocomposites, treatments of heavy metal contaminants, heterogeneous catalysis and also in components of active corrosion protection coatings. In this study, organosilane-modified mesoporous were prepared and investigated by various physico-chemical techniques, including X-ray powder diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), ^{13}C CP/MAS NMR and Thermalgravimetry (TGA). The organically modified mesoporous derived from the reaction of mesoporous Si-MCM-41 with trimethylchlorosilane have been considered. The results indicated that the surface modification did not modify the original structure of Si-MCM-41 but altered their original hydrophilic nature to hydrophobic. Herein, we demonstrate the possibility of modify and functionalize surface of MCM-41, enabling applications in many fields as nanocomposites, drug releasing agents and components of active coatings.

Keywords: MCM-41, Trimethylchlorosilane, Functionalized

1. Introduction

The preparation of mesoporous materials family M41S since 1992 (Kresge, et al., 1992) until now has opened a wide field of applications (Lazaridis, et al., 2009; Zhao, et al., 1996; Corma, 1997). Mesoporous molecular sieves have relatively large and uniform pore size (15-100 Å), which break past the pore size constraint (< 15 Å) of microporous zeolites, high surface areas (> 1000 m²·g⁻¹), highly ordered pore structures and very narrow pore size distributions (Juang, et al., 2006). Such materials have been prepared using cationic surfactant species to produce mesoscopically ordered lamellar (MCM-50), hexagonal (MCM-41), or cubic (MCM-48) structures in approximately micrometer-sized domains (Hoffmann, et al., 2006).

As one of these materials, MCM-41 is characterized by high pore volume, moderate hydrophobic character as well as parallel and ideally shaped pore structures without the complications of a network. Mesoporous silica can be synthesized via polycondensation of silica species which originate from different sources of silica such as sodium silicate, fumed silica or tetraethylorthosilicate (TEOS) and Ludox in the presence of surfactants as

structure-directing agents. Many types of ionic surfactant such as hexadecyltrimethylammonium bromide and non-ionic surfactants such as amphiphilic triblock copolymers have been used for obtaining mesoporous silica with different pore structure and morphological characteristics.

Mesoporous silicas have been functionalized with both inorganic and organic species in order to provide additional physical or chemical properties to the silica parent material. These new hybrid organic-inorganic mesoporous ordered structures have attracted increasing attention because of their high surface area and the functionalized pore channels of large diameter. The high surface area allows the binding of a large number of surface groups and the functionalized pore channels of large diameter allow an easy reaction with adsorbates. The grafting of the functional groups to the pore walls of the mesoporous adsorbents can be fulfilled by the reaction between the hydrolyzable moieties and the surface silanol groups of the mesostructures.

In general, functionalization of these materials can be carried out by two independent methods (Lim & Stein, 1999). The first of them is carried out by grafting the surface of the preformed silica by means of silanol groups reactions with an organoalkoxysilane compound supporting the active functional group. The second method consists in the simultaneous co-condensation within the synthesis medium of the alkoxysilane precursor of the silica mesostructure and a selected organoalkoxysilane to obtain the functionalized material after one step.

In this study, mesoporous pure silica Si-MCM-41 was chemically modified by functionalization with trimethylchlorosilane (TMCS). The synthesized material were investigated by various physico-chemical techniques, including X-ray powder diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR), ^{13}C CP/MAS NMR and Thermalgravimetry (TGA). The results indicated that the surface modification did not modify the original structure of Si-MCM-41 but altered their original hydrophilic nature to hydrophobic.

2. Experimental

2.1 Preparation of mesoporous pure silica Si-MCM-41

The parent Si-MCM-41 was synthesized according to the following procedures. First, sodium silicate in a clear solution was prepared by dissolving 30.0450 g of Ludox (30 wt% SiO_2) in 3.0000 g of aqueous sodium hydroxide 1 M solution (pellet from Merck) and heated at 80 °C for two hours. The surfactant solution was prepared by dissolving 9.1115 g of cetyltrimethylammonium bromide (CTABr) purchased from BDH Analar and 1.0500 g of 25 wt% aqueous NH_3 solution (Merck) in a polypropylene bottle and the mixture was then heated with stirring for one hour at 80 °C. After cooling to room temperature, sodium silicate was added dropwise to a polypropylene bottle containing surfactant solution. The tightly closed bottle was stirred vigorously at room temperature before heating in oven at 97 °C for one hour in static condition. pH adjustment to 10.2 by dropwise addition of acetic acid 25 wt% (CH_3COOH) (Merck) was performed and resulting gel mixture was heated for two days. Gel mixture had a molar composition of 6 SiO_2 : 1 CTABr : 1.5 Na_2O : 0.15 $(\text{NH}_4)_2\text{O}$: 250 H_2O . After two days, siliceous MCM-41 was filtered, washed with distilled water until it neutralized and dried in an oven at 97 °C for 16 hours. The template was removed through calcination in air under static conditions at 550 °C for six hours before further application.

2.2 Modification of Si-MCM-41

A mixture of 1.5 g of as-synthesized MCM-41 and 54 mL of trimethylchlorosilane (TMCS) was refluxed at 45 °C for overnight. 27 mL of pyridine was added and refluxed for another 18 hour. The resulting solid was then filtered, washed with hexane and absolute ethanol and dried.

2.3 Characterization

The solid samples were identified by powder XRD using a Bruker D8 Advance Diffractometer with Cu-K_α radiation ($\lambda = 0.15418$ nm) at 40 kV and 40 mA. The FTIR spectra of the solid samples prepared by KBr technique were recorded on Shidmadzu Fourier Transform Infrared spectrometer. In this technique a pinch of sample was mixed with KBr salt and pelletized and IR spectra of the pellet were taken. Thermal stability of the samples was measured by using Pyris Diamond TG/DTA-Perkin Elmer under nitrogen flow (35 mL/min) with heating rate 20 °C/min from room temperature to 900 °C. Solid State ^{13}C CP/MAS NMR experiments were performed using Bruker Advance 400 MHz 9.4 T spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with a recycle delay of 5.0 s, number of transient of 6000 and spinning rate of 7 kHz. Chemical shifts for ^{13}C was referred to TMS. Thermo Finnigan - Surface Area Analyzer instrument was used for the single point BET surface area analysis. It's been done at 77 K (boiling temperature of liquid nitrogen) to determine surface area. Prior to the determination of single point BET surface area, the sample was out gassed at 200 °C for 20 minutes.

3. Results and discussion

3.1 Powder X-ray Diffraction (XRD)

The X-ray Diffraction patterns obtained for siliceous MCM-41 before and after calcination in air at 550 °C are given in Figure 1. The diffractogram in Figure 1(a) shows the presence of a single high intensity and three weak peaks. In the low 2-theta region of 1.5° – 10°, the XRD pattern exhibits four diffraction peaks which could be indexed as (100), (110), (200) and (210) reflections, respectively. This is characteristics of long range ordered hexagonal MCM-41 mesoporous phase. The parent MCM-41 exhibits a narrow and strong peak at 41.03 Å which is corresponding to a lattice parameter, $a_0 = 47.03$ Å and other three weak peaks at 23.76 Å, 20.55 Å and 15.74 Å due to the (100), (110), (200) and (210) reflections, respectively.

The presence of same peaks in the siliceous MCM-41 after calcination with the increasing significantly the intensity of (100) peak and d_{100} value shifted to the higher value shows that the removal of organic surfactant template and condensation of silanol groups in the pore walls. This can lead to the rearrangement of silica walls of siliceous MCM-41 thus increased the crystallinity of MCM-41. Kleitz, *et al.* reported that an initial change occurred up to 250 °C with the increase in intensity for all XRD reflections which indicate the increasing of crystallinity (Kleitz, *et al.*, 2001). Calcination of Si-MCM-41 containing large amounts of carbonaceous species can leave carbon deposits or coke as contaminant in the pores and pore blocking may occur. When the surfactant template is removed by calcination, the low angle reflection intensities increase and the mesoporous ordered structure could be dramatically affected (Kleitz, *et al.*, 2003).

Figure 2 shows diffractogram of siliceous MCM-41 modified by silylation with trimethylchlorosilane (TMCS). The four main peaks still remained even after silylation process with increasing the intensity of (100) peak. This suggests that long range order of mesopores is still preserved and the silylation has no adverse effects on the ordered mesoporous structure of MCM-41. This shows also that TMCS only interacts on to the surface of calcined siliceous MCM-41. The XRD pattern is in excellent agreement with the parent MCM-41 which suggests that highly ordered MCM-41 can still be obtained after calcination and modification by silylation with TMCS.

3.2 Fourier Transform Infrared (FTIR) Spectroscopy

The FTIR spectra of siliceous MCM-41 before and after calcination and the modified product by silylation with trimethylchlorosilane (TMCS) are illustrated in Figure 3. For parent MCM-41, bands observed at 1234.3 cm⁻¹ and 1071.4 cm⁻¹ are characteristics peaks of asymmetric Si-O-Si stretching. Another characteristics peak is the symmetric Si-O-Si stretching observed at 785.9 cm⁻¹. The peak at 456.1 cm⁻¹ is characteristic of Si-O-Si bending. The broad band around 3500 cm⁻¹ may be due to surface silanols and adsorbed water molecules which indicating the silica framework is hydrophilic.

For calcined siliceous MCM-41, the disappearance of peak at 2922.9 cm⁻¹ and 2852.5 cm⁻¹ can be concluded that the calcination at 550 °C is complete. This indicates that the organic template has been removed completely due to calcination. MCM-41 tends to adsorb water vapours in air since the surface of silica framework is water liking, the stretching mode of H₂O is observed at 1635.5 cm⁻¹. From the silylated spectrum, we can see the existence new peak around 2965.4 cm⁻¹ characteristics of CH of methyl group. The stretching mode at 846.7 cm⁻¹ and 758.9 cm⁻¹ characteristics of Si-C stretching vibrations which are absent in the spectrum of siliceous MCM-41 before and after calcination. The presence of these new peaks indicates that there is interaction between TMCS and silanol group on wall surface of MCM-41. This suggest that the -Si(CH₃)₃ groups have successfully grafted onto the surface of MCM-41 which this can increases the hydrophobicity of Si-MCM-41 to facilitate the threading of any organic material into the channel of MCM-41.

3.3 ¹³C CP/MAS Solid-state NMR

From the spectrum in Figure 4, only single and sharp peak was observed at -1.111 ppm corresponds to carbon of methyl group in TMCS that anchored on the silica surface of Si-MCM-41 (Sutra, *et al.*, 1999; Bu & Rhee, 2000). The existence of one peak indicates that local environment of carbon of methyl group in TMCS is same. The result of the ¹³C CP/MAS NMR study has proved that trimethylsilyl groups have been successfully grafted onto the Si-MCM-41. It also showed that the organic surfactant template has been removed completely due to calcination as there is no other peaks exist.

3.4 Thermogravimetric Analysis (TGA)

Figure 5 (a) shows the TGA profiles of the siliceous MCM-41 in nitrogen atmosphere showing three stages of weight loss. The first weight loss was observed at 50-150 °C about 3.1031 % due to desorption of physisorbed water on the external surface of the crystallites or occluded in the macropores and mesopores present between

the crystallites aggregates (Selvaraj, et al., 2003; Chu, et al., 2003). Meanwhile, in the range of 150-330 °C weight losses about 30.9060% are attributed to the decomposition or removal of organic (Guo, et al., 2001; He, et al., 2000). At the temperature range 330 - 550 °C is due to residual surfactant decomposition and water loss from the condensation of adjacent silanol group to form siloxane bond about 4.5197%. The total weight loss up to 900 °C of this sample is in 39%. There was almost no weight loss after 550 °C indicating that surfactant had been removed completely.

Figure 5 (b) shows the TGA profiles of calcined siliceous MCM-41. There is no significant difference in the curve pattern in the thermogram collected. Although water absorbed was detected in FTIR analysis was broader but thermogravimetric analysis shows little mass loss about 0.4231% after given thermal treatment. At higher temperatures (above 100 °C), the mass loss (0.6731%) can still be observed although the template have been removed. This could be due to the decomposition of coke but the loss was too small indicating that the sample was stable towards heat.

Figure 5 (c) shows the TGA profiles of silylated MCM-41 which shows weight loss under 100 °C about 0.9883% due to loss of physisorbed water molecules. The very gradual degradation rate observed at temperatures over the range between 100 to 550 °C corresponds to removal of the TMCS groups attached to Si-MCM-41 (Kang & Choi, 2000). Meanwhile, further decomposition was observed after 550 °C due to the thermal dehydroxylation of internal surface silanol groups to form siloxane bridges about 4.0993%. The adsorbed water on the external surface for the parent MCM-41 was approximately more 3% and less than 1% after silylation treatment. This can confirm the hydrophobicity enhancement obtained by replacing surface silanol groups with trimethylsilyl groups (Jeong, et al., 2000).

3.5 BET surface area

The specific BET surface areas of as-synthesized calcined and silylated Si-MCM-41 are summarized in Table 1. The surface area for all the samples were determined by single-point BET method. The results show that the surface area of Si-MCM-41 was significantly increased after calcinations (1083.54 m²/g). This may due to the removal of the organic template, CTABr, which resulted in an increase in the adsorption site for the nitrogen molecules and hence the surface area of the calcined Si-MCM-41 sample (Shylesh & Singh, 2004). The finding is well in agreement with the XRD, FTIR and TGA which also give indications of the removal of organic template from the material. On the other hand, the surface area of silylated Si-MCM-41 decreased to 975.42 m²/g with respect to that of the calcined sample as expected if the surface silanol groups were replaced by the larger trimethylsilyl groups. The silylation by trimethylchlorosilane may have induced the trimethylsilyl groups to occupy defect sites in the pore wall as self-assembled monolayers and decreased the adsorption site for the nitrogen molecules contributing to the decrease in surface area. The result also suggests that the silylation treatment has not altered the ordered structure of Si-MCM-41 as has been shown by the XRD pattern depicted in Figure 2.

4. Conclusion

Siliceous MCM-41 was successfully synthesized from Ludox (30 wt% SiO₂) as silica sources. Preparation and characterization of silylated Si-MCM-41 have been carried out. Silylated Si-MCM-41 was synthesized by modification by silylation with trimethylchlorosilane (TMCS).

XRD study reveals that the framework of silylated Si-MCM-41 was not destroyed and the long-range order was found to increase upon silylation. The very slight shifting of the main peak (100) to higher 2θ° for calcined and silylated Si-MCM-41 indicates the removal of the organic surfactant template and incorporation of the trimethylsilyl groups, respectively. It also revealed from FTIR spectroscopy and ¹³C CP/MAS NMR that there is interaction between TMCS and silanol group of wall surface of Si-MCM-41.

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Table 1. BET surface areas for as-synthesized, calcined and silylated samples of Si-MCM-41.

Sample	S _{BET} (m ² /g)
As-synthesized Si-MCM-41	687.36
Calcined Si-MCM-41	1083.55
Silylated Si-MCM-41	975.42

The specific BET surface areas of as-synthesized, calcined and silylated Si-MCM-41. The surface area for all the samples were determined by single-point BET method.

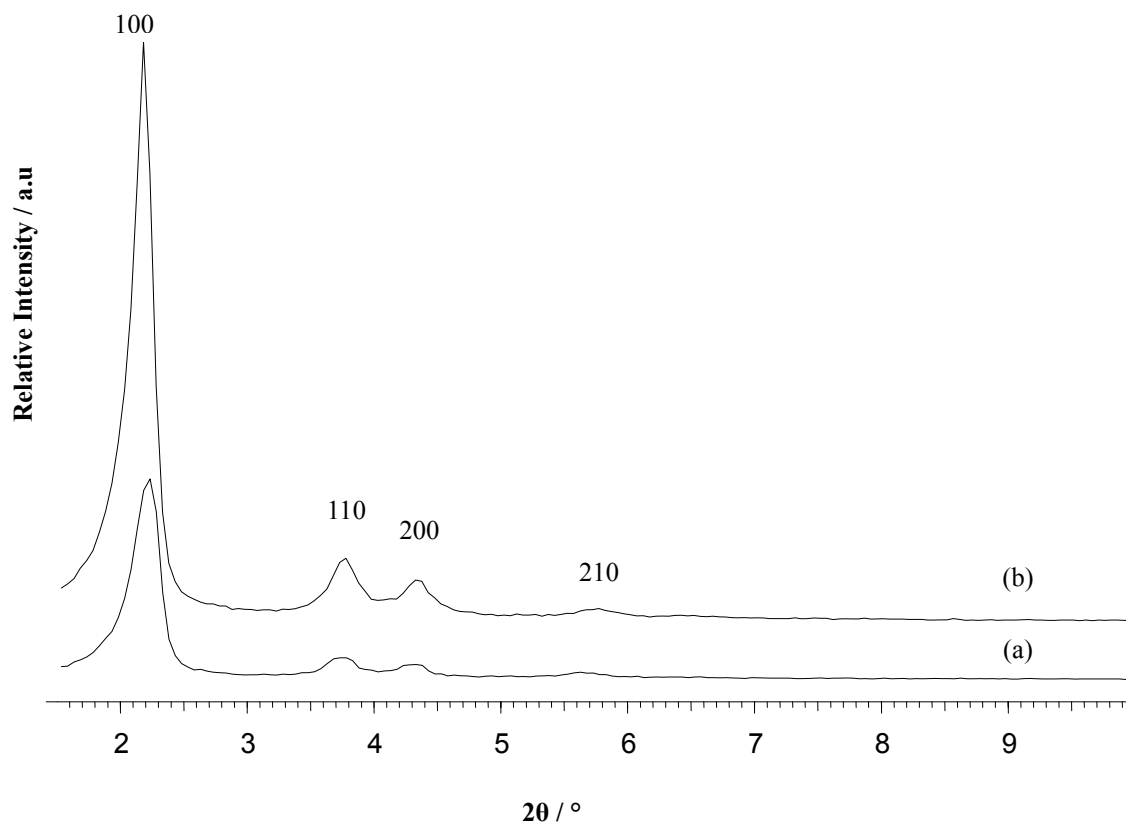


Figure 1. XRD patterns for (a) siliceous MCM-41 and (b) calcined siliceous MCM-41 at 550 °C in air. The X-ray Diffraction patterns for siliceous MCM-41 before and after calcinations in air at 550 °C. The XRD pattern exhibits four diffraction peaks which could be indexed as (100), (110), (200) and (210) reflections, respectively. This is characteristic of long range ordered hexagonal MCM-41 mesoporous phase.

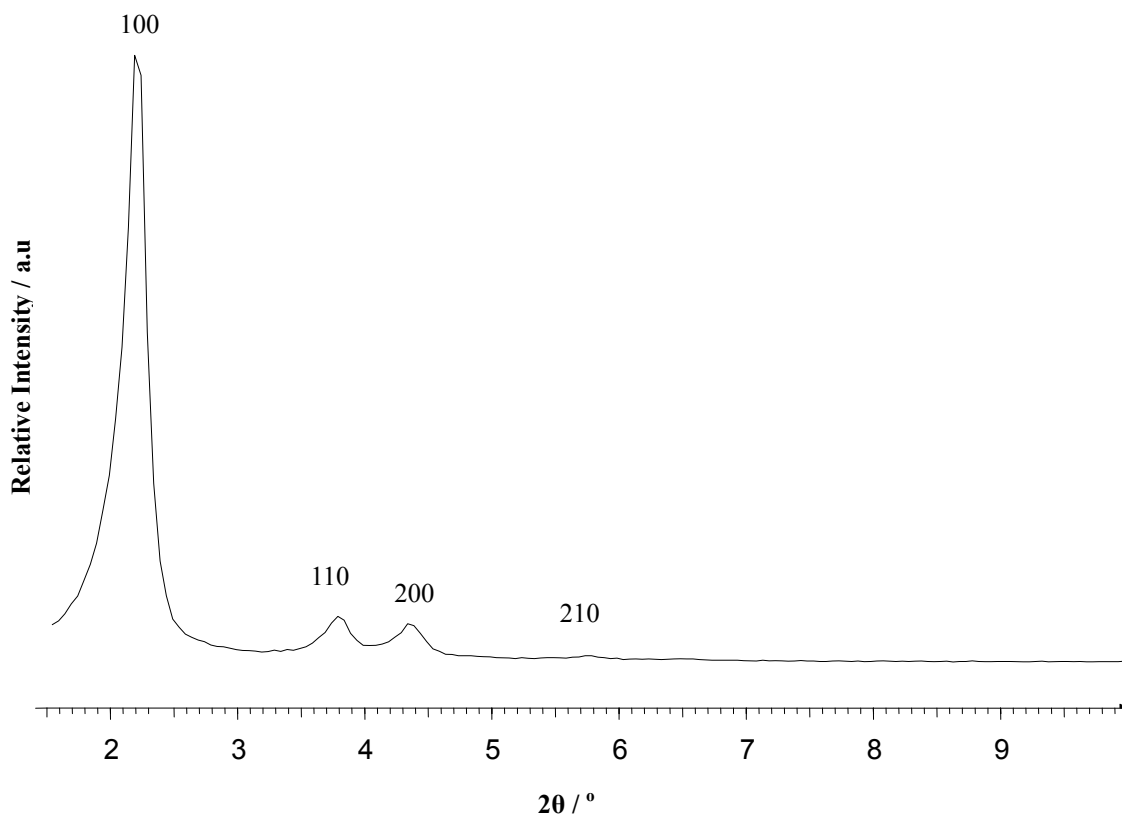


Figure 2. XRD pattern for silylated Si-MCM-41 obtained by modification by silylation with TMCS

The four main peaks still remained even after silylation process with increasing the intensity of (100) peak. XRD patterns suggests that long range order of mesopores is still preserved and the silylation has no adverse effects on the ordered mesoporous structure of MCM-41 and TMCS only interacts on to the surface of calcined siliceous MCM-41.

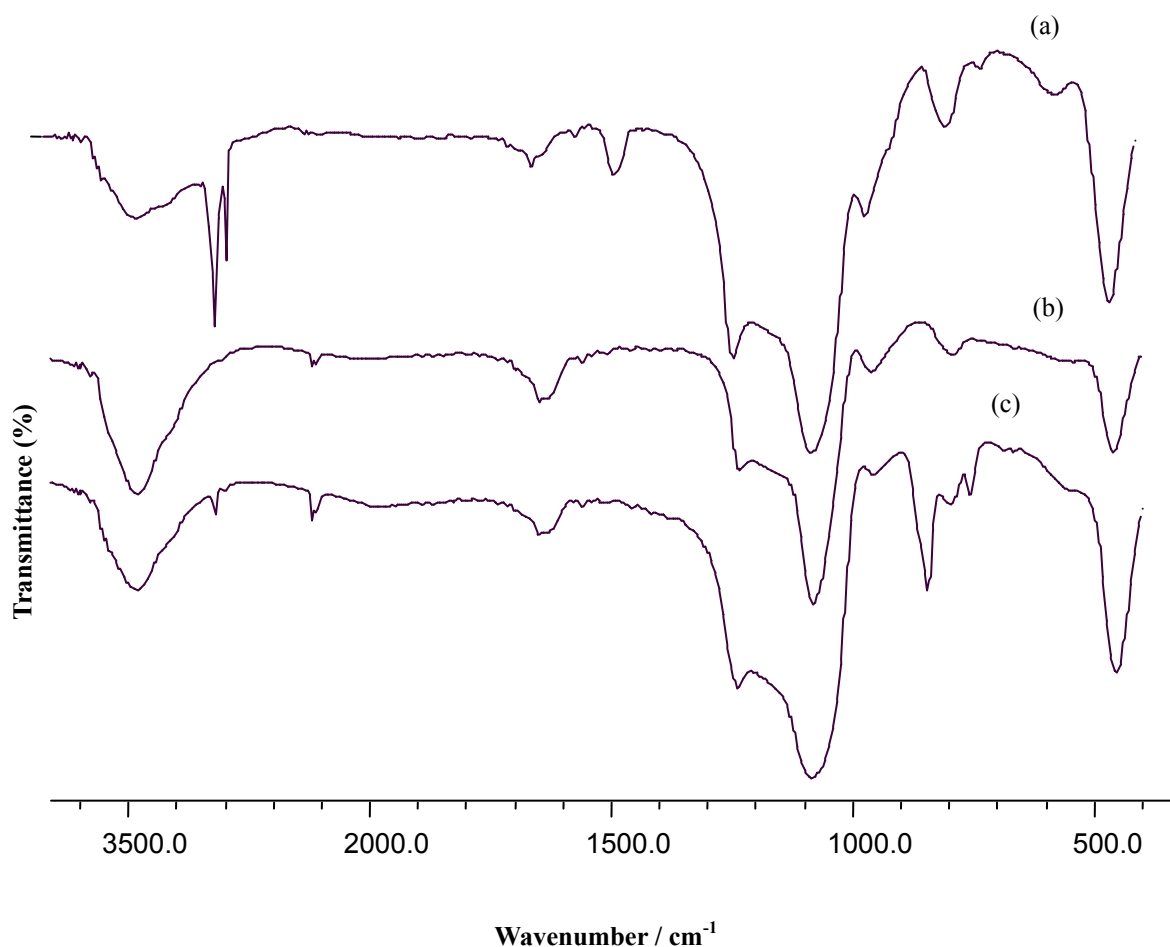


Figure 3. FTIR spectra for (a) siliceous MCM-41, (b) calcined siliceous MCM-41 and (c) silylated Si-MCM-41. The FTIR spectra of siliceous MCM-41 before and after calcination and the modified product by silylation with trimethylchlorosilane (TMCS) are illustrated in Figure 3. For calcined siliceous MCM-41, the disappearance of peak at 2922.9 cm^{-1} and 2852.5 cm^{-1} can be concluded that the calcination at $550\text{ }^{\circ}\text{C}$ is complete. From the silylated spectrum, the presence of new peaks indicates that there is interaction between TMCS and silanol group on wall surface of MCM-41.

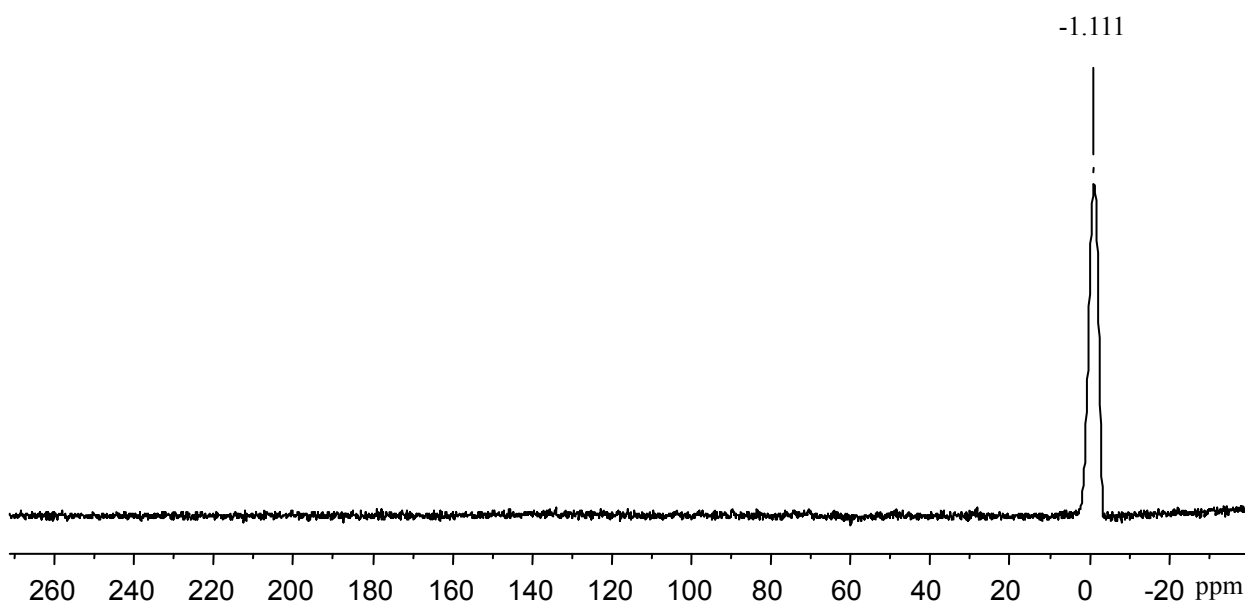


Figure 4. ^{13}C CP/MAS NMR spectrum for silylated Si-MCM-41

The existence of one peak corresponds to carbon of methyl group in TMCS that anchored on the silica surface of Si-MCM-41 which indicate that trimethylsilyl groups have been successfully grafted onto the Si-MCM-41.

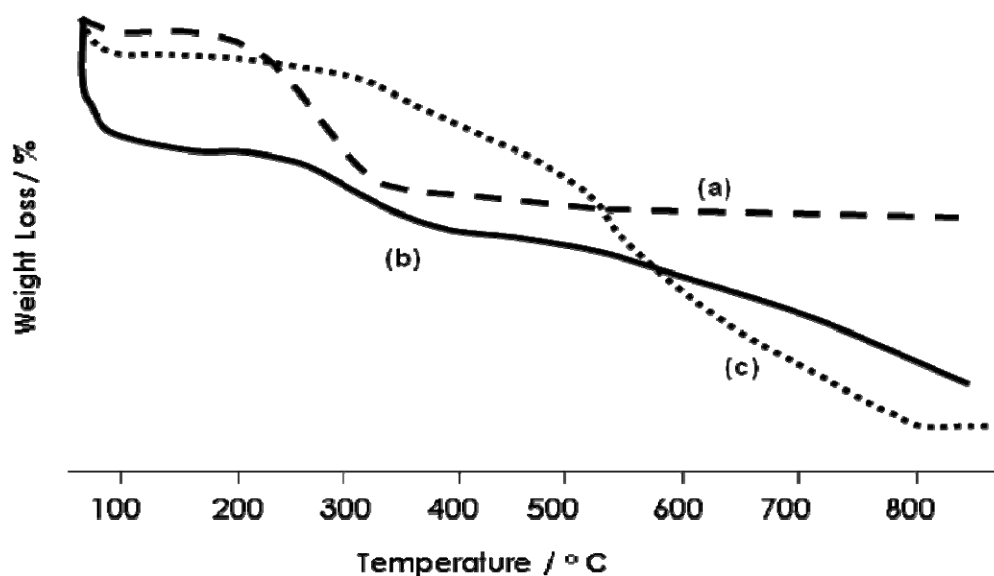


Figure 5. TGA curve of (a) siliceous MCM-41, (b) calcined Si-MCM-41 and (c) silylated Si-MCM-41 in nitrogen atmosphere from 40 °C to 900 °C at 20.00 °C/min

Figure 5 shows the TGA profiles of the (a) siliceous MCM-41, (b) calcined Si-MCM-41 and (c) silylated Si-MCM-41 in nitrogen atmosphere showing three stages of weight loss. The first weight loss due to desorption of physisorbed water on the external surface of the crystallites or occluded in the macropores and mesopores present between the crystallites aggregates. At the temperature range 330-550 °C is due to residual surfactant decomposition and water loss from the condensation of adjacent silanol group to form siloxane bond. Meanwhile, further decomposition was observed after 550 °C due to the thermal dehydroxylation of internal surface silanol groups to form siloxane bridges.