

Original Research Paper

# Thermogravimetric Analysis (TGA) Profile at Different Calcination Conditions for Synthesis of PTES-SBA-15

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**Abstract:** The aim of this work is to study the effects of calcination condition on the properties of mesoporous silica, SBA-15 modified with phenyl group of organosilane. Functional group SBA-15 were synthesized and hydrothermally aged. The surfactant template was conventionally removed by calcination at varied temperature and duration. Thermogravimetric Analysis (TGA) was employed to characterize the pure and modified SBA-15. The TGA profile presented here would include modified SBA-15 functionalized using two different methods, direct-synthesis and post-grafting. The characterization profile from TGA showed that the temperature of calcination has large influence in determining the effectiveness of surfactant removal and incorporation of alkoxy silane into pure silica whether by post-grafting or direct synthesis method. However, the duration of calcination does not significantly affect these characteristics. Besides, mesoporous structure of SBA-15 by post-grafting method shows higher degree of functionalization than that of direct-synthesis.

**Keywords:** Calcination, Direct-Synthesis, Post-Grafting, Phenyltriethoxysilane, SBA-15, Thermogravimetric Analysis

## Introduction

Porous solid is extensively used as catalyst and adsorbent due to their high surface area. Typical porous material, zeolite has been widely used because of their uniform pore size distribution and good stability (Rowell and Yaghi, 2004). However, zeolite has small pores size and this limits their application involving large reactant molecule. A new material with larger pore called Santa Barbara Amorphous-15 (SBA-15) has been of recent interest. This type of mesoporous silica with amorphous, hexagonal shape and two-dimension has characteristics of narrow pore size distribution, thermally stable, inert, harmless and cheap (Wua *et al.*, 2006). Their thick wall leads to high thermal and mechanical stability. This make them desirable for catalytic application since catalyst are always exposed to high temperature and steam (Filiz and Aysen, 2012). However, the disadvantage of SBA-15 that restricts them from behaves effectively as catalyst is their low acidity strength (Norhasyimi *et al.*, 2010). To overcome this problem, SBA-15 is modified by incorporating functional group consists of organosilane such as Vinyltriethoxysilane (VTES), phenyltriethoxysilane (PTES) and Methyltriethoxysilane (MTES) to the structure of SBA-15.

Direct-synthesis is one of the methods to functionalize SBA-15. It involves co-condensation of silica source such as Tetramethylorthosilicate (TMOS) and Tetraethylorthosilicate (TEOS) together with functional group organotrialkoxysilane. This method can be done under neutral, acidic and or alkaline condition. It is an expensive method since it involves large volume of organosilanes. For post-grafting method, the silica is synthesized using same procedure as direct-synthesis and then the free silanol will react with organosilane. Compared to direct synthesis, grafting of pores only take place on outer surface. Grafting of pores in direct synthesis occur both in inner and outer place of pores. Use of post-grafting compared to direct-synthesis resulting in ordered structure and higher hydrothermal stability (Garcia *et al.*, 2007). Although the uses of post-grafting to synthesis mesoporous 3D-hexagonal organosilicate films produce more well-ordered structure, the porosity of silica is reduced (Matheron *et al.*, 2006). Besides that, direct-synthesis results in homogenous distribution of organic group over the surface while post-grafting presents better defined pore sizes (Calvoa *et al.*, 2009).

Modified SBA-15 using PTES produces particle with more uniform size and shape (Wua *et al.*, 2006). One of

significant characteristics of PTES is its hydrophobic nature of phenyl group. This hydrophobic nature can be improved by adjusting ratio of phenyl loading and grafting phenyl loaded sample with trimethylchlorosilane (Gokulakrishnana *et al.*, 2013). Due to its hydrophobic characteristics, PTES particle shows low water vapour adsorption (Wua *et al.*, 2006) and small weight loss during TGA analysis (Gokulakrishnana *et al.*, 2013). Because of incorporation of hydrophobic molecule, the hydrothermal stability of membrane can be improved (Li *et al.*, 2011). PTES modified silica also results in large pore size but low hydrogen permeances (Li *et al.*, 2011).

Properties of SBA-15 can be amended by factors like hydrothermal treatment, reaction temperatures, surfactants removal and stirring time. They play important roles in determining the wall thickness, pore size and morphology characteristics of mesoporous material. This property affects the hydrothermal and mechanical stability which are imperative for their application in catalysis. A work by Benamor *et al.* (2012) concluded that the factors that strongly affect the structure of SBA-15 are silica condensation rate and surfactant behaviour which are dependent on temperature and duration at ripening and aging step (Benamor *et al.*, 2012). Another research found that the mesoporous diameter and volume of SBA-15 is increased by treatment of heat in aging steps (Klimovaa *et al.*, 2006). Synthesis by using two thermal treatment steps especially the second step are proved to increase the pore size, wall thickness and decrease in microporosity (Brodie-Lindera *et al.*, 2008; Ko and Ryong, 2000).

Surfactants are amphiphilic molecule that is used as structure directing agents. It determines the pore structure and morphological characteristics of SBA-15. These surfactants must be removed to obtain pure solid. It is an essential aspect in deciding the final properties of product. Although there are other alternatives such as chemical removal, washing with ethanol and reflux extraction, the conventional method of surfactant removal is used in this study. The duration and temperature of calcination play important roles in template removal in which carrying out calcination at high temperature may waste large amount of used organic template, produce smell and toxic gases (Huang *et al.*, 2005). Therefore, TGA profile in this study is important to understand the calcination parameter towards incorporation of phenyl group into SBA-15 mesostructure as well as the effectiveness of surfactant removal at different synthesis methods to achieve economical procedure of obtaining better properties of modified SBA-15 in catalysis application.

## Methodology

### Materials

Pluronic 123 triblock copolymer [poly(ethylene oxide)<sub>20</sub>-poly(propyleneoxide)<sub>70</sub>-poly(ethylene oxide)<sub>20</sub>] (P123), tetraorthosilicate (TEOS), 2M hydrochloric acid (HCl), phenyltriethoxysilane (PTES), toluene, *p*-toluenesulfonic acid (PTSA).

### Synthesis of Pure SBA-15

About 4g of P123 was dissolved in 125mL of 2M HCl at room temperature. After complete dissolution, the mixture was heated to 40°C on hotplate and 8.6g of TEOS was added. The solution was stirred for 20h and the temperature was maintained at 40°C. Then, the white precipitate was hydrothermally aged in oven at 100°C for 24h. The product was recovered and dried. The surfactant was removed by calcination in static air at 550°C for 5h using furnace.

### Synthesis of PTES-SBA-15 by Direct-Synthesis

About 4g of P123 was dissolved in 125mL of 2M HCl at room temperature. After complete dissolution, the mixture was heated to 40°C on hotplate and 8.6g of TEOS was added. PTES was added in TEOS:PTES molar ratio of 15:1. The solution was stirred for 20h and the temperature was maintained at 40°C. Then, the white precipitate was hydrothermally aged at 100°C for 24h in oven. The product was recovered and dried. The surfactant was removed by calcination in static air using furnace. During calcination, the temperature was varied for 350 and 550°C and the duration was varied for 3h and 5h.

### Synthesis of PTES-SBA-15 by Post-Grafting

About 1g of SBA-15 and 150 mL toluene were dissolved in 3 flask equipped with mechanical agitator. The dissolved mixture was stirred for 30 min. at 50°C. 0.007g of PTSA and PTES were added in TEOS:PTES molar ratio of 15:1. After stirring for 2 h, the sample was filtered and hydrothermally aged at 100°C for 24h in oven. Calcination was carried out in static air using furnace. The calcination temperature was varied for 450 and 750°C.

### Characterization

TGA was conducted in presence of nitrogen as inert purge with flow of 100 mL min<sup>-1</sup> and heating rate of 10°C/min, heating from 20 to 900°C.

## Results and Discussion

TGA is used to measure the weight loss during heating of sample. It can determine the presence of material containing carbon, hydrogen, oxygen on the surface of silica such as surfactants (Giaquinto, 2012).

TGA also can detect the amount of alkoxysilane group incorporated to pure SBA-15 sample. The alkoxysilane in this case is PTES.

Pure SBA-15 in Fig. 1 shows an initial weight loss from 30 to 100°C. Above 100°C, very small weight loss was identified. This shows that SBA-15 has good thermal stability within the temperature range.

Figure 2 shows the functionalization of SBA-15 using direct synthesis at different temperature and calcination duration time while Fig. 3 shows the TG curve of functionalization of SBA-15 using post-grafting method. Both samples of functionalized SBA-15 in Fig. 2 and 3 show good thermal stability, good term with thermal properties of pure SBA-15. All samples showed weight loss at temperature 30-100°C due to loss of moisture. Samples also shows weight loss at temperature above 100°C for different method of synthesis and different calcination temperature as well as calcination duration time. These differences are further elaborated at Fig. 4 until Fig. 7, in which the amount of loss are clearly depicted by weight loss percentage.

#### *TGA Profile of PTES-SBA-15 at Different Calcination Temperature using Direct-Synthesis*

Figure 4a and b display the TG curve of pure SBA-15, PTES-SBA-15 calcined at 550°C and 350°C. Samples were labeled as PTES-SBA-15(550) and PTES-SBA-15(350) respectively. All samples were calcined for 3 h.

For temperature range of 25 to 150°C, all three samples show a significant weight loss which was due to loss of adsorbed water. According to Wua *et al.* (2006) the weight loss below 150°C was due to water evaporation. The weight loss for PTES-SBA-15 sample during first region does not differ much with pure SBA-15. This proved the hydrophobicity of phenyl group present in PTES functionalized silica. Small weight loss indicates that the water adsorbed in the material is less due to hydrophobic characteristic of PTES. However, when comparing the functionalized sample with pure sample, both functionalized sample exhibit higher weight loss than the pure SBA-15. This could be due to the removal of unreacted phenyl group of PTES present in functionalized sample (Li *et al.*, 2011).

Most of surfactants (P123) decompose between 150 to 250°C (Johansson, 2010). This is also in accordance with the result analyzed by (Kruk and Jaroniec, 2001). It is stated that, under nitrogen atmosphere, ionic surfactant template in pure silica usually decompose completely at much lower temperature, below 300°C (Ko and Ryong, 2000). Hence, the weight loss for temperature range of 150 to 300°C as shown in TG curve from Fig. 4 is due to the decomposition of surfactants.

From Fig. 4. a and b, it is shown that PTES-SBA-15(350) exhibit higher weight loss than PTES-SBA-15(550) due to decomposition of surfactants. This indicates that the remaining surfactants are not being removed efficiently at calcination temperature of 350°C. The surfactants are still remain in sample PTES-SBA-15(350). Therefore, it can be concluded that, calcination at 550°C are more efficient in removing surfactant compare to at 350°C.

For temperature range of 300 to 800°C, the weight loss is due to decomposition of organic group (Wua *et al.*, 2006). Both SBA-15 and PTES-SBA-15(550) do not show significant weight loss while the PTES-SBA-15(350) shows a significant weight loss. This significant weight loss is contributed to the decomposition of phenyl group PTES anchored onto the silica surface. It can be hypothesized that functionalization of phenyl group into SBA-15 is more effective at temperature 350°C compare to that of 550°C.

#### *TGA Profile of PTES-SBA-15 at Different Duration Time of Calcination by Direct-Synthesis Method*

Figure 5a and b show the TGA profile of PTES-SBA-15 of different duration calcination time by direct-synthesis method. Functionalized sample calcined for 5 h is indicated by PTES-SBA-15(5) while functionalized sample calcined for 3 h is indicated by PTES-SBA-15(3). The first region of mass loss was due to evaporation of water occurred within temperature range of 25 to 150°C. The weight loss of PTES-SBA-15(3) is higher than PTES-SBA-15(5) in these range. This is due to the decomposition of remaining PTES that are unreacted during synthesis.

For TG curve region between 150 to 300°C, the weight loss of PTES-SBA-15(5) is slightly higher than PTES-SBA-15(3). This could be due to the amount of surfactant of PTES-SBA-15(5) decomposed at calcination duration is higher than PTES-SBA-15(3).

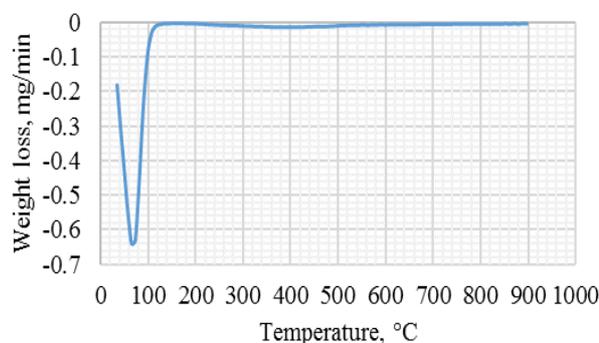


Fig. 1. TG curve for pure SBA-15

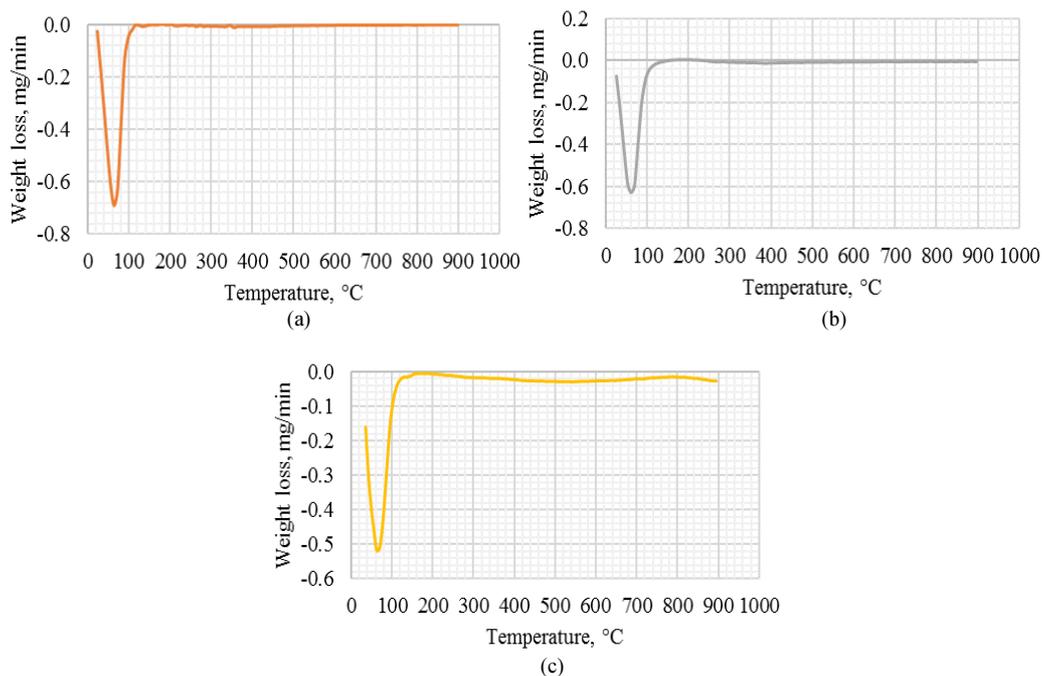


Fig. 2. TG curve for PTES-SBA-15 using direct synthesis at (a) calcination 550°C for 5 hours (b) calcination 550°C for 3 hours and (c) calcination 350°C for 3 hours

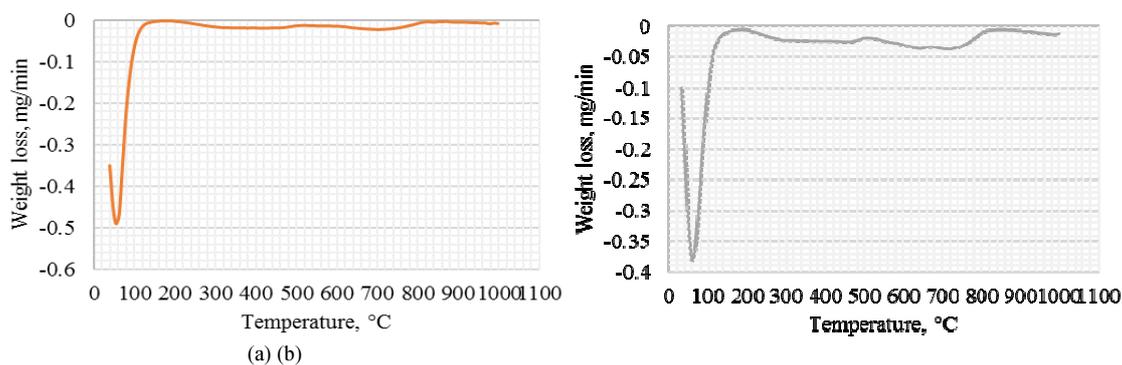


Fig. 3. TG curve for PTES-SBA-15 using post-grafting at (a) calcination at 450°C (b) calcination at 750°C

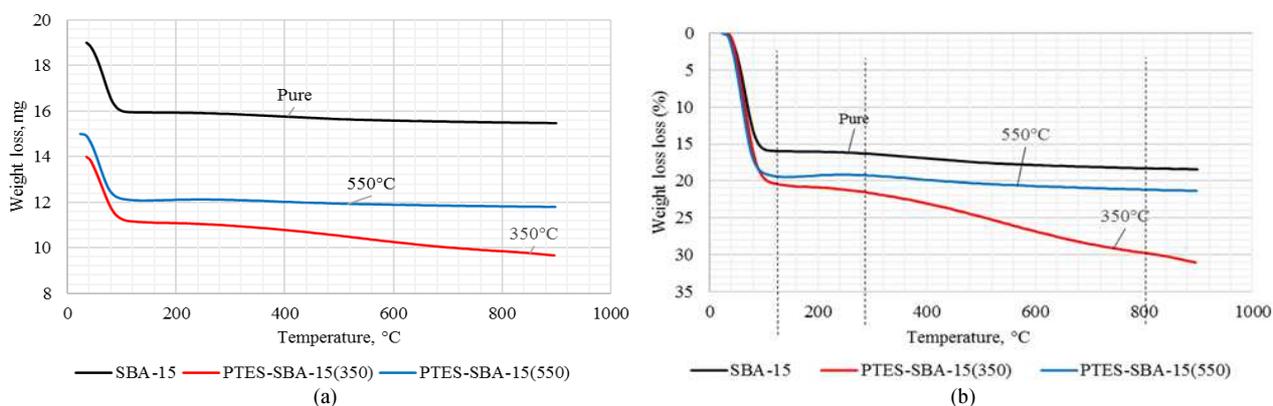


Fig. 4. (a) Weight loss curves of PTES-SBA-15 of different curing temperature using direct-synthesis (b) Weight loss percentage curves of PTES-SBA-15 of different curing temperature using direct-synthesis

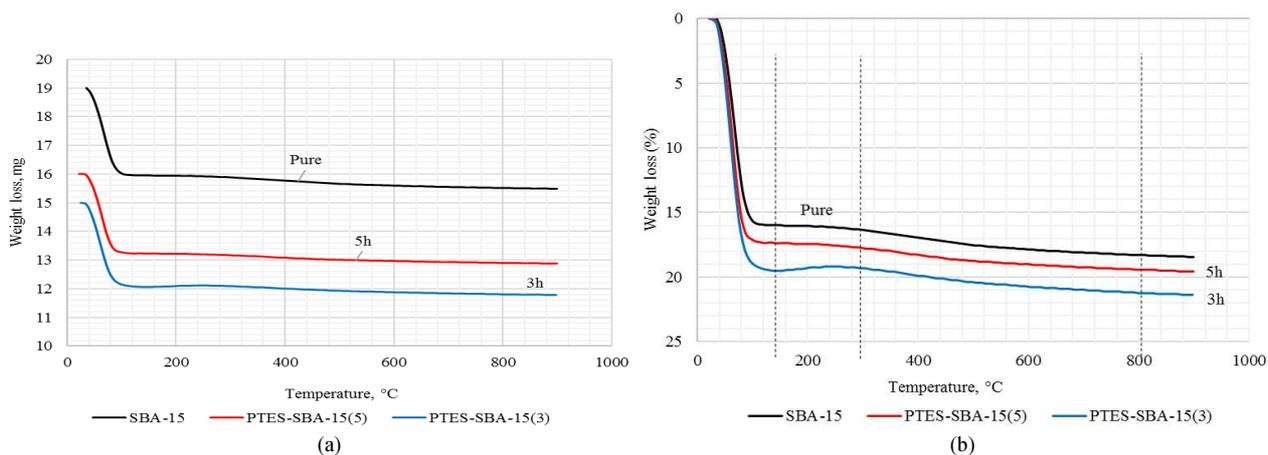


Fig. 5. (a) Weight loss curves of PTES-SBA-15 of different calcination duration time using direct-synthesis (b) Weight loss percentage curves of PTES-SBA-15 of different calcination duration time using direct-synthesis method.

However, it can be concluded that the duration time of calcination does not significantly influence the effectiveness of surfactant removal due to insignificant difference of weight loss displayed from TG curve.

For region between 300 to 800°C, the weight loss of both functionalized samples does not much differ from pure SBA-15. The decomposition of PTES is very small which indicates that phenyl group does not effectively incorporate into the surface of SBA-15 in this study. It can be concluded that the duration time of calcination does not significantly affect the effectiveness of phenyl group incorporation into SBA-15 mesostructure.

#### TGA Profile of PTES-SBA-15 at Different Calcination Temperature by Post-Grafting Method

The region between 25 to 150°C for Fig. 6 shows higher weight loss for pure SBA-15 than functionalized sample. This indicates that the content of adsorbed water of pure SBA-15 is higher than PTES-SBA-15(450) and PTES-SBA-15(750) due to the absence of functional group which could hinder the water adsorption by mesostructure.

For region with temperature range of 150 to 300°C, the weight loss of PTES-SBA-15(750) shows equal amount to PTES-SBA-15(450). This could be explained by the same amount of unremoved surfactant at calcination temperature of 450 and 750°C. This may conclude that for post grafting method, calcination temperature above 450°C is effective for surfactant removal process.

A higher weight loss is observed for region at temperature ranged 300 to 800°C than other regions. PTES-SBA-15(750) shows the highest weight loss indicating that high amount of phenyl group decompose at this region. It can be hypothesized that

phenyl group was effectively incorporated at higher calcination temperature by using post-grafting method into the mesostructure of SBA-15.

#### TGA Profile of PTES-SBA-15 at Different Method of Functionalization

Figure 7a and b compares TGA profile of PTES-SBA-15 for different method of functionalization. PTES-SBA-15(P) indicates the functionalization by post-grafting while PTES-SBA-15(D) by direct synthesis method. Both methods undergo calcination at temperature of 550°C.

For temperature 25 to 150°C, PTES-SBA-15(P) shows lower weight loss compared to pure SBA-15 and PTES-SBA-15(D). This was probably due to small amount of adsorbed water contained in PTES-SBA-15(P). PTES-SBA-15(D) shows higher weight loss which could be attributed to decomposition of some unreacted PTES during synthesis of material.

PTES-SBA-15(P) shows higher weight loss than PTES-SBA-15(D) at TG curve region of temperature 150-300°C. Therefore, it can be concluded that removal of surfactant by calcination is more effective by direct synthesis method.

PTES-SBA-15(P) shows higher weight loss than PTES-SBA-15(D) in the region of 300-800°C due to higher decomposition of phenyl group, PTES and less than 1% weight loss at temperature at above 800°C, which could be attributed to phenyl group functionalized in deeper internal microstructure of SBA-15. This indicates that post-grafting method exhibits better incorporation of phenyl group in internal mesostructure surface of SBA-15 (García *et al.*, 2007). Direct method shows lower degree of functionalization as the weight loss is not much differ from pure SBA-15.

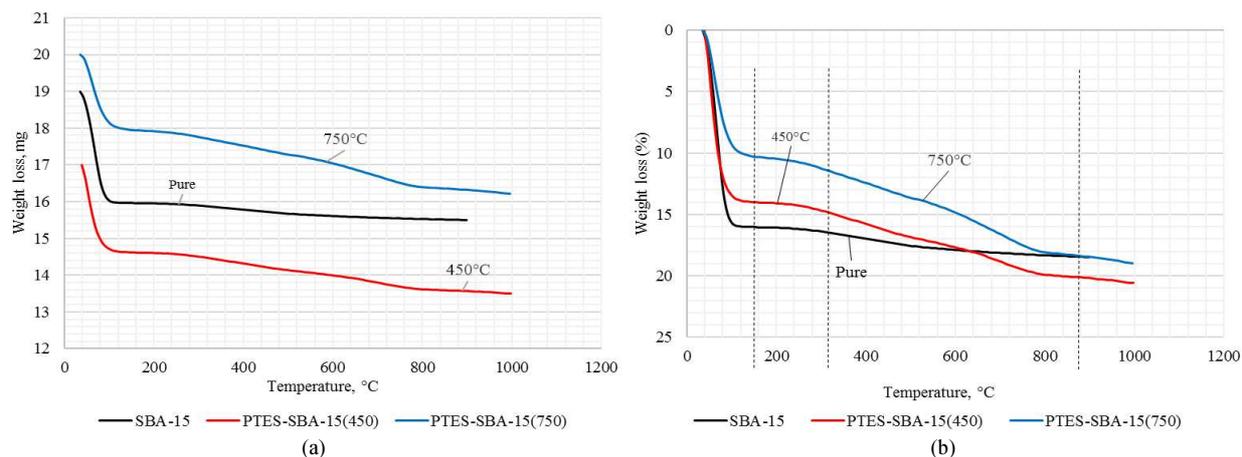


Fig. 6. (a) Weight loss curves of PTES-SBA-15 of different calcination temperature using post-grafting (b) Weight loss percentage curves of PTES-SBA-15 of different calcination temperature using post-grafting

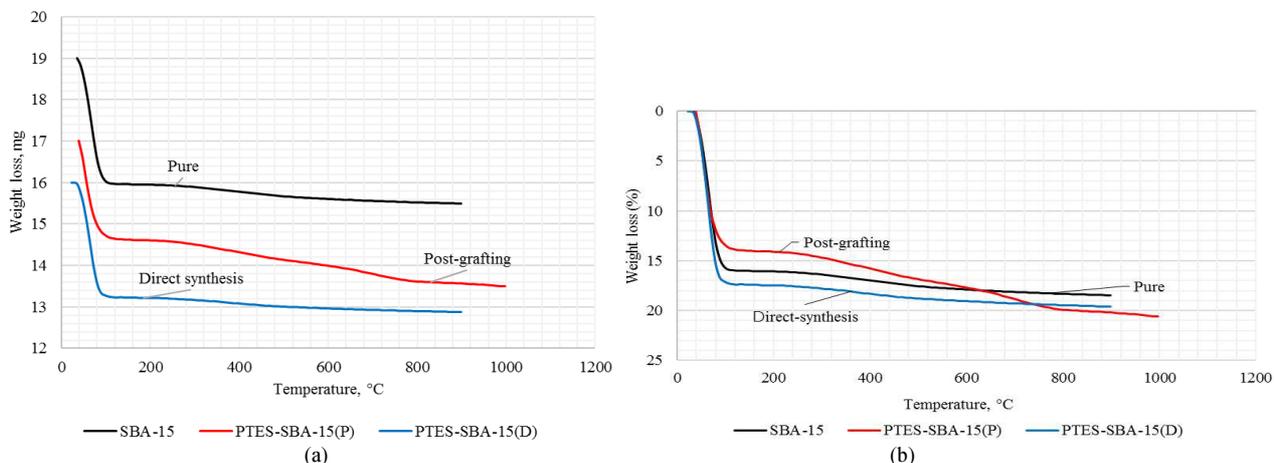


Fig. 7. (a) Weight loss curves of PTES-SBA-15 of method of functionalization (b) Weight loss percentage curves of PTES-SBA-15 of different method of functionalization

## Conclusion

It can be concluded that, for direct synthesis method, the different temperature of calcination could affect the effectiveness of surfactant removal and amount of PTES incorporated into SBA-15. Calcination at lower temperature of 350°C provides higher degree of functionalization. Duration of calcination, however, does not largely influence the effectiveness of surfactant removal and incorporation of PTES. This finding for direct synthesis method is contradict with post-grafting method in which the results of calcination at higher temperature, 750°C shows larger amount of PTES able to be incorporated into internal surface of SBA-15.

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## Author's Contributions

**Norhasyimi Rahmat:** Principal investigator who design the experiment and lead the investigation.  
**Nurjihan Sadon:** Research assistant.  
**Muhammad Abeed Yusof:** Research assistant.

## Ethics

This study is investigated to observe the effect of calcination temperature and duration time characterized by thermal analysis, which is being explored for this range temperature and time with specific silica

precursor. This study is not replicated or duplicated from any other study. In fact, this study would contribute to further understands and acknowledge the importance of thermal analysis towards different properties of catalysts.

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