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THERMOGRAVIMETRIC ANALYSIS (TGA) PROFILE OF MODIFIED SBA-15 AT DIFFERENT AMOUNT OF ALKOXYSILANE GROUP

(Profil Thermografimetrik Analisis SBA-15 Berfungsi Pada Jumlah Kumpulan Alkoxysilane Yang Berlainan)

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Abstract

This study focused on mesoporous silica SBA-15 modified with alkoxysilane functional group; phenyltriethoxysilane (PTES) and vinyltriethoxysilane (VTES) using direct synthesis and post-grafting methods. By direct synthesis method, SBA-15 templated by triblock copolymer (P123) and functionalized with alkoxysilane groups at different amount of loadings were co-condensed with tetraethyl orthosilicate (TEOS) under acidic conditions. As for post-grafting method, different loadings of alkoxysilane groups were added after co-condensation of TEOS with P123 template. Both synthesis methods used calcination process to remove surfactant template at 550°C for 5 hours. The derivatized SBA-15 was characterized by thermogravimetric analysis to evaluate the profile at different loadings of alkoxysilane groups with different synthesis method. At temperature range of 300°C-800°C, post-grafting method displayed the highest weight loss of phenyl and vinyl groups. However, there was no significant difference of weight loss for different amount of organosilane groups. In this study, TGA has shown to be significant characterization means to determine the effects of different method used in synthesizing modified SBA-15. It was shown that different loading of phenyl and vinyl groups did not affect the efficiency of surfactant removal.

Keywords: characterization, thermogravimetric analysis, direct synthesis, post-grafting, modified SBA-15, mesoporous silica

Abstrak

Kajian ini ditumpukan kepada silika mesoporus, SBA-15, yang difungsikan dengan kumpulan alkoxysilane; phenyltriethoxysilane (PTES) dan vinyltriethoxysilane (VTES) menggunakan kaedah sintesis langsung dan pos-grafting. Melalui sintesis langsung, SBA-15 yang ditemplatkan oleh triblok kopolimer (P123) dan difungsikan oleh kumpulan alkoxysilane pada jumlah berlainan telah dikondensasikan bersama tetraethyl orthosilicate (TEOS) dalam keadaan berasid. Dengan kaedah pos-grafting pula, jumlah kumpulan alkoxysilane yang berlainan ditambahkan hanya selepas kondensasi TEOS pada templat P123. Kedua-dua kaedah ini menggunakan proses pembakaran untuk menyesarkan templat surfaktan pada suhu 550°C selama 5 jam. Derivatisasi SBA-15 telah diperincikan oleh thermografimetrik analisis untuk menilai profil pada jumlah kumpulan alkoxysilane yang berlainan bagi teknik yang berbeza. Pada rangkuman suhu 300°C-800°C, kaedah pos-grafting telah menunjukkan kehilangan berat kumpulan phenyl dan vinyl yang paling tinggi. Namun begitu, tiada perbezaan kehilangan berat yang ketara didapati pada jumlah kumpulan alkoxysilane yang berlainan. Dalam kajian ini juga, TGA telah membuktikan kepentingannya sebagai kaedah perincian untuk menentukan kesan teknik sintesis kefungsian SBA-15 yang berbeza. Telah dibuktikan juga bahawa jumlah kumpulan phenyl dan vinyl yang berlainan tidak memberi kesan terhadap efisiensi penyingkiran surfaktan.

Kata kunci: perincian, analisis thermografimetrik, sintesis langsung, pos-grafting, SBA-15 berfungsi, silika mesoporus

Introduction

Santa Barbara Amorphous-15 (SBA-15) is one of the unique mesoporous structures that have uniform hexagonal array of pores with limited pore size distribution and pore diameter of between 5 and 15 nm [1]. The thickness of the framework walls is about 3.1 to 6.4 nm, which gives SBA-15 advantage on hydrothermal and mechanical stability. It also has high internal surface area of 400 to 900 m^2, which makes SBA-15 as a good choice for use in many applications [2]. Pure silica SBA-15 showed very limited catalytic activities due to the lack of lattice defect, redox properties, basicity and acidity. There have been many ways to increase the active sites and improve the catalytic activity by introducing guests into the framework of SBA-15, in which the effect of surface modification has not been rigorously investigated. Specifically, there are two accesses to produce organic functionalization of SBA-15, which are (i) post grafting method and (ii) direct synthesis method [3].

Direct synthesis is a method used to functionalize SBA-15 which involving one-step co-condensation of tetraalkoxysilanes such as tetraethyl orthosilicate (TEOS) with organosilanes prepare under basic or neutral or near-neutral pH condition during functionalization [4] while post-grafting method consists of reaction of a organosilane with surface silanol groups using an appropriate solvent under reflux conditions. This method is actually the first method to be used to modify mesoporous silica materials. The silanol groups react with the organosilane to form a layer of covalently coupled surface functional groups [5].

The use of organosilanes organic groups gives the resulting materials many favorable features to broaden the application fields. In this regard, vinyl and phenyl functionalities are hypothesized to exhibit ample reactivity and display versatile precursor moieties for both subsequent organic transformations and metal incorporation reactions. Thus, the introduction of such reactive groups on the SBA-15 could keep a sufficiently large pore volume, makes the material very interesting for catalytic and sensing applications [6].

Thermogravimetric analysis or thermal gravimetric analysis (TGA) is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). Thermogravimetric analysis is a useful tool to determine the presence of material containing carbon, hydrogen, and oxygen on the surface of silica such as surfactants (in the case of templated silicas) and bonded alkyl groups. This method can also yield quantitative results as the weight loss is accurately measured by an internal microbalance, and the percent weight of a sample lost through thermal decomposition can be calculated [7]. This characterization technique has been used in various environmental, food, pharmaceutical and petrochemical applications [8].

Since the discovery of mesoporous materials, numerous studies on modified SBA-15 has been done due to its specialty to be used in various applications. However, study on TGA profile of alkoxysilane modified SBA-15 has yet to be widely explored. Thus, in this study, the characterization of modified SBA-15 using the TGA technique is employed for different methods of post-grafting and direct synthesis.

Materials and Methods

Materials

Pluronic 123 triblock copolymer [poly(ethylene oxide)$_{20}$–poly(propyleneoxide)$_{70}$–poly(ethylene oxide)$_{20}$] (P123), tetraorthosilicate (TEOS), 2M hydrochloric acid (HCl), phenyltriethoxysilane (PTES), toluene, *p*-toluenesulfonic acid (PTSA).

Synthesis of Pure SBA-15

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 and VTES-SBA-15 using direct synthesis

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 1: 5 and 1:15.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 at 550°C for 5 hours.

Synthesis of PTES-SBA-15 and VTES-SBA-15 using post-grafting

1g of SBA-15 and 150mL toluene were dissolved in 3 flask equipped with mechanical agitator. The dissolved mixture was stirred for 30 minutes at 50°C. 0.007g of PTSA and PTES were added in TEOS: PTES molar ratio of 1:5 and 1:15. After stirring for 2 hours, the sample was filtered and hydrothermally aged at 100°C for 24h in oven. Calcination was carried out in static air using furnace at 550°C for 5 hours.

Characterization

Characterization was conducted using TGA 4000 Brand Perkin Elmer in the presence of nitrogen as inert purge with flow of 100mL/min and heating rate of 10°C/min, heating from 20°C to 900°C.

Results and Discussion

Direct synthesis of phenyl modified SBA-15. Figure 1 shows different loading of PTES-SBA-15 functionalizes using direct-synthesis. At starting temperature to 150^{o}C, a phenomenon of release of water formed from condensation process in silica is happened. At this range, the water loss varies from 16-21% for different type of samples.

Surfactant tends to be decomposed at temperature range of 150^{o}C to 300^{o}C. All samples show low percentage of surfactant decomposition, which indicates that surfactant have been efficiently removed during calcination. Further weight loss at temperature range 300oC to 800oC is due to the decomposition of organosilane groups as reported by Kruk et al. [2]. With this regard, sample both samples PTES:TEOS 5:1 and 15:1 have shown to have 2-2.5% weight loss of phenyl groups.

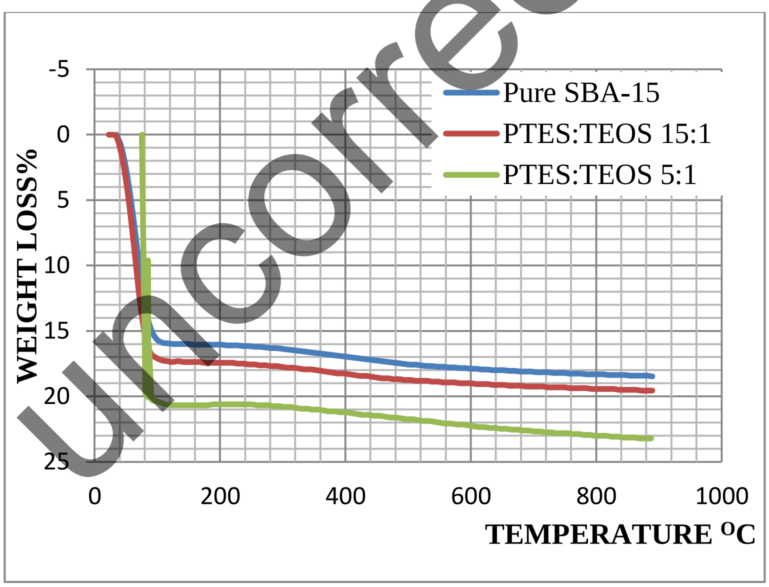

Figure 1. Different loading of phenyl group to synthesize modified SBA-15 using direct-synthesis method.

Post-grafting of phenyl modified SBA-15

Figure 2 shows the comparison of different loading of phenyl group functionalized with SBA-15 using post-grafting method. At temperature range of 25^{o}C to 150^{o}C, evaporation of water for pure SBA-15 is about 16.05%, which is the highest. Evaporation of water for PTES:TEOS 15:1 and PTES:TEOS 1:5 are about 10.40% and 5.13%, respectively.

Weight loss occurs for all samples after 150°C to 800°C due to decomposition of surfactant and organosilane groups. However, all samples show very least of surfactant weight loss at temperature 150°C to 300°C. This could be due to calcination condition that completely decompose and remove the templating surfactant from mesopore framework. Small difference of weight loss at range of 300°C and 800°C is observed between PTES:TEOS 5:1 and PTES:TEOS 15:1 which are at respective 6.34% and 6.9% weight loss.

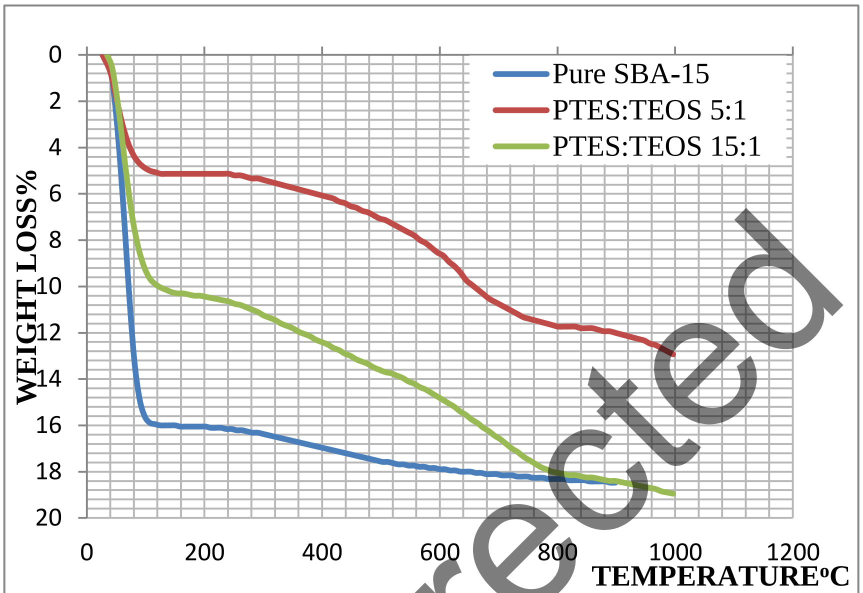

Figure 2. Different loading of phenyl group to synthesize modified SBA-15 using post-grafting method.

As shown in Figure 3, two sets of different methods were carried out to functionalize SBA-15. In the first set, SBA-15 was functionalized using direct-synthesis while the second set using post-grafting. Both sets of sample have same loading phenyl-group being attached in silica mesopores framework.

At temperature range of 300°C to 800°C, sample of phenyl group functionalized by post grafting shows a higher weight loss compare to sample functionalized by direct synthesis. Sample post-grafting 15:1 has 6.8% while sample post-grafting 5:1 has 6.3% weight loss. Samples from direct synthesis 15:1 and 5:1 show only 2.1% and 2.6% weight loss. At this amount of phenyl group loading, it could be predicted that phenyl-group is efficiently incorporated into silica mesoporous framework using post-grafting compare to direct-synthesis method.

Direct synthesis of vinyl modified SBA-15

In comparison with pure SBA-15, VTES-SBA-15 (ratio 5:1) exhibit higher weight loss than pure SBA-15. The difference of weight loss of pure SBA-15 and VTES-SBA-15 is due to the amount of vinyl group incorporated.

The surfactant (P123) decomposes at temperature range from 150 to 300ºC. Kruk et al. [2] has shown similar pattern of result when analyzing the TGA profile of calcined SBA-15 [2]. It is claimed that major weight loss in this temperature range is due to desorption of surfactant template. Based on Figure 4, all three samples show the same trend in weight loss, which indicates that the decomposition of remaining surfactant in those three samples do not affected by different amount of vinyl group during calcination process.

In accordance with the work of Lim et al. [9], this study also displays decomposition of VTES group at temperature between 280 and 440ºC [9]. Small difference of weight loss is observed between VTES: TEOS 5:1 and VTES:TEOS 15:1 which are at 2.5% and 1.35% respectively.

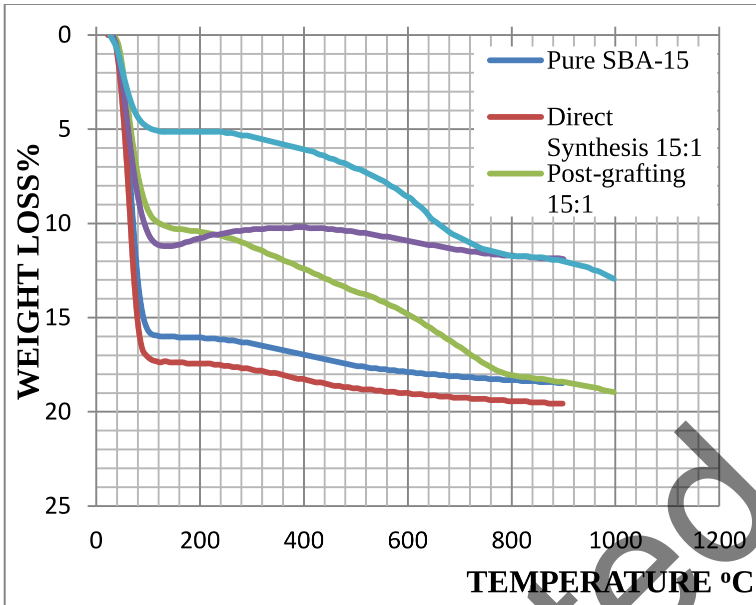

Figure 3. Different methods of synthesizing PTES-SBA-15

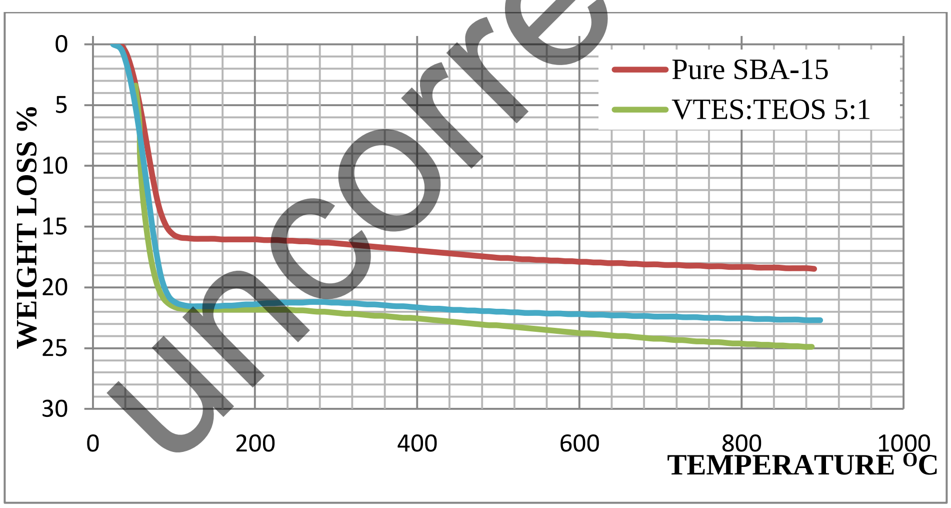

Figure 4. Different loading of vinyl group to synthesize modified SBA-15 using direct-synthesis method.

The effects of methods on the functionalization of VTES-SBA-15

Figure 5 shows the TGA profile of VTES-SBA-15 using different method of functionalization, which is direct synthesis and post-grafting. Both methods have gone through the same calcinations process at 550 ^{o}C for 5 hours.

In the temperature range from 30 to 150^{o}C, sample VTES-SBA-15 prepared from direct synthesis method shows the highest weight loss as compared to VTES-SBA-15 by post grafting. This could be due to the amount of water adsorbed in the mesoporous structure during direct synthesis is higher compare to post-grafting method. For the temperature range between 150-280^{o}C, VTES-SBA-15 by direct synthesis shows equally the same weight loss with

VTES-SBA-15 by post-grafting, which is 0.5-0.64%. This shows that different methods do not affect the surfactant removal process.

At the range of 280-440^{o}C, VTES-SBA-15 by post-grafting shows a higher value of weight loss than VTES-SBA-15 by direct synthesis due to higher amount of vinyl group decomposition. This also indicates that more triethoxyvinylsilane groups are attached to SBA-15 mesoporous structure by post-grafting method.

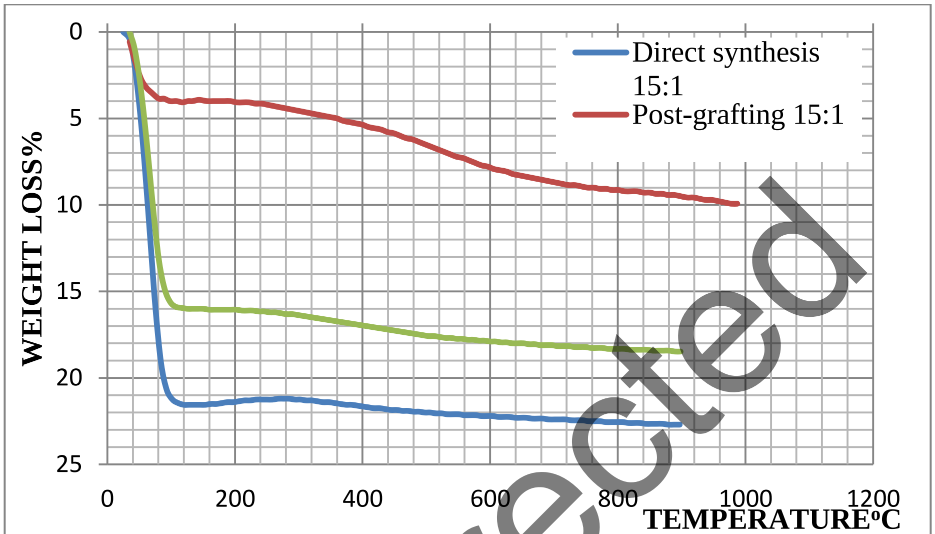

Figure 5. Different methods of synthesizing VTES-SBA-15

Conclusion

In this study, direct-synthesis and post-grafting method used to synthesize different loading of phenyltriethoxysilane and vinyltriethoxysilane into SBA-15 mesoporous structure using TGA analysis has been successfully demonstrated. Both methods of synthesizing both types of organosilane functionalized SBA-15 do not influence the process of surfactant template removal. There is no significant weight loss observed for different amount functionalized with SBA-15 in this scope of work. However, TGA analysis displays a significant difference of weight loss on different methods used to functionalize SBA-15 for both PTES and VTES functional group.

Acknowledgement

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