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Preparation of Fe_3O_4/SiO_2-guanidine organobase catalyst for 1,5-diphenylpenta-2,4-dien-1-one synthesis

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Abstract. A novel heterogeneous organobase catalyst of Fe_3O_4/SiO_2-guanidine was prepared in three stages. First, Fe_3O_4 nanoparticle was obtained by co-precipitation method using seaweed *Sargassum* Sp. as natural reductant. Fe_3O_4 was then coated by SiO_2 using TEOS as silica source, resulting Fe_3O_4/SiO_2. Finally, Fe_3O_4/SiO_2-Guanidine was obtained by modifying Fe_3O_4/SiO_2 with guanidine in the suitable reaction condition. This organobase catalyst was characterized by Scanning Electron Microscope (SEM), Energy Dispersive X-ray Spectroscopy (EDS), and Particle Size Analyzer (PSA). The material was then used as a highly active catalyst in aldol condensation reaction between acetophenone and cinnamaldehyde to produce 1,5-diphenylpenta-2,4-dien-1-one. The structure elucidation of the organic product was confirmed by UV-Vis, FTIR, and LC-MS.

1. Introduction

Recently, the development of heterogeneous catalysts for various organic transformations became a trending topic. Fe_3O_4 based heterogeneous catalysts were widely applied in the synthesis of organic compounds with specific functional groups, such as Fe_3O_4/SiO_2-metformin [1], Fe_3O_4/SiO_2-urea [2], and Fe_3O_4/SiO_2-NH_2 [3] magnetic catalyst. The wide range applications of mostly heterogeneous catalysts are interesting because they can be easily separated from the reaction mixture by an external permanent magnet due to the presence of catalyst's magnetic properties [1].

In this study, Fe_3O_4 nanoparticle was obtained by reducing the ferric chloride solution with seaweed *Sargassum* Sp. as a reducing agent and efficient stabilizer (capping agent) [4] and by adding ferrous chloride which also acts as a reducing agent [1-3]. The reaction was then followed by silica coating and guanidine functionalization of Fe_3O_4 to form Fe_3O_4/SiO_2-guanidine which will be used in the synthesis of 1,5-diphenylpenta-2,4-dien-1-one compound by aldol condensation reaction between acetophenone and cinnamaldehyde.The catalyst has amino group that can be associated with its basic properties. The basic catalyst can extract the H-α atom of acetophenone in Aldol condensation mechanism [5]. From the previous research regarding the basic properties of the catalyst, we hope that Fe_3O_4/SiO_2-guanidine catalysts can be used as an alternative heterogenous catalyst for aldol condensation reaction to replace NaOH as the conventional catalyst for this reaction [5, 6].

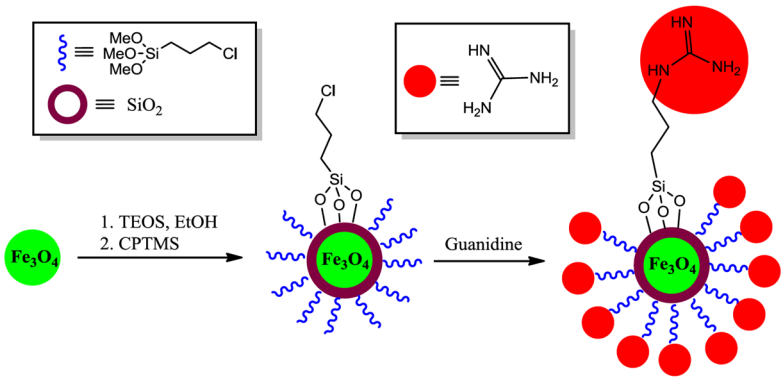


Figure 1. Illustration of the prepared catalyst

2. Materials and methods

2.1. General

Chemicals used were pro-analytical grade. The *Sargassum* Sp. was collected from Binuangeun Sea in Banten, Jawa Barat, Indonesia.

2.2. Preparation of magnetic nanoparticles (Fe_3O_4)

In a 1 L beaker glass, 1 mmol of $FeCl_3.6H_2O$, 0.25 mmol of $FeCl_2.4H_2O$, 5 mL of *Sargassum* extract, and 50 mL of deionized water were stirred at room temperature, while NaOH was added instantaneously to adjust to pH 10. After 2 hours, the product was filtered and washed with deionized water and alcohol, then dried at 60°C [1, 2].

2.3. Preparation of silica-coated magnetic nanoparticles (Fe_3O_4/SiO_2)

In a 1 L beaker glass, 1 g of Fe_3O_4 was dissolved by adding water (20 mL), ethanol (60 mL), and ammonia (2 mL, 25 wt.%). The resulting dispersion was then homogenized by ultrasonic bath. Then, the solution of TEOS (0.5 mL)in ethanol (10 mL) was added to the dispersion. Followed by stirring for 16 h, the obtained solid product was colleted by an external magnetic and washed with ethanol. Finally, the product was dried at 60°C [7].

2.4. Preparation of Fe_3O_4/SiO_2-Guanidine

In a 250 mL of round bottom flask, 1 mL (5 mmol) of 3-chloropropyl-trimethoxysilane (CPTMS) was dissolved in 100 mL of dried toluene. This mixture was added to 1 g of Fe_3O_4/SiO_2 and the solution was stirred for 18 h at 60°C. The obtained solid product (Fe_3O_4/SiO_2-Cl) was washed with toluene, separated by a magnet, and dried at 60°C. Then, it was used in the following step to synthesize Fe_3O_4/SiO_2-guanidine. 1 g of Fe_3O_4/SiO_2-Cl and KI (1.66 g, 10 mmol) were added to a solution of guanidine hydrochloride (0.59 g, 10 mmol) and K_2CO_3 (1.38 g, 10 mmol) in acetonitril (50 mL) in a round-bottom flask and the mixture was stirred under reflux condition for 8 h. The obtained solid product was then separated by a magnet and washed with water followed by drying at 80°C [1,2]. Illustration of the prepared catalyst was depicted in figure 1.

2.5. Synthesis of 1,5-diphenylpenta-2,4-dien-1-one

A mixture of cinnamaldehyde (5 mmol), acetophenone (5 mmol), and Fe_3O_4/SiO_2-guanidine (20% weight) in ethanol was stirred for 10 h at 75°C. After completion of the reaction, the catalyst was separated by an external magnet. The obtained solid product was filtered and washed with water and hexene, then the solid product was purified by recrystallization using hot methanol.

3. Results and discussion

The morphology of Fe_3O_4/SiO_2 was also characterized by using SEM as shown in figure 2(b). The surface differences between these two compounds indicated that the Fe_3O_4 was successfully coated with silica.

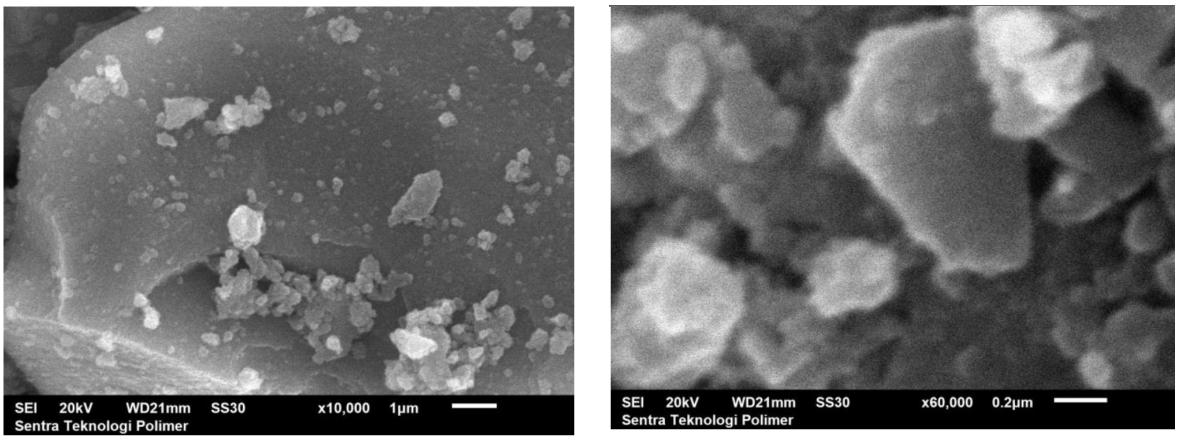
The presence of Fe and O elements as the fundamental components of Fe_3O_4 was investigated using EDS spectra as shown in Table 1. EDS analysis for Fe_3O_4/SiO_2 showed the element contained in this compound were Fe, O and Si, indicated that the silica was successfully coated on Fe_3O_4.

Figure 3 shows the particle size of Fe_3O_4, Fe_3O_4/SiO_2 and Fe_3O_4/SiO_2-guanidine characterized by PSA are 35, 159, and 257 nm, respectively. The increasing of particle size was affected by the silica coating and guanidine functionalization of the Fe_3O_4.

The Fe_3O_4/SiO_2-guanidine was then applied in synthesis of 1,5-diphenylpenta-2,4-dien-1-one compound by aldol condensation reaction between acetophenone and cinnamaldehyde. Figure 4 is the reaction scheme for the synthesis. The reaction was carried out with the suitable condition using 20% weight of catalyst at 75°C for 10 hours. The purity of the product was analyzed by using the thin layer chromatography with ethyl acetate:n-hexane(1:4) as the solvent. The yield product obtained was 42 %.

The active site of the Fe_3O_4/SiO_2-guanidine catalyst was $-NH_2$ which acted as a Bronsted-Lowry base that can take the acidic hydrogen from substrates. This site was very suitable for the nucleophilic attack. The other active site of the catalyst was Fe^{3+} which showed a Lewis acid behavior and it can react with the carbonyl groups of cinnamaldehyde to accelerate the conjugation (process) [3].

The structure elucidation of the 1,5-diphenylpenta-2,4-dien-1-one product was confirmed by UV-Vis, FTIR and LC-MS. The UV-Vis spectrum shows the maximum wavelength is 336 nm that confirmed with the appearance of the yellowish crystal product. The FTIR spectrum shows the presence of C-H



(a) (b)

Figure 2. SEM images of Fe_3O_4/SiO_2 with (a) 10,000 × and (b) 60,000 × magnification.

Table 1. EDS analysis of the catalyst.

Element	Composition (% wt)	
	Fe_3O_4	$Fe_3O_4 – SiO_2$
C	10.29 ± 3.11	9.44 ± 1.91
O	33.24 ± 11.58	28.66 ± 6.71
Fe	54.65 ± 15.60	54.92 ± 8.17
Na	1.32 ± 1.07	0.00 ± 00
Si	0.00 ± 0.00	6.98 ± 0.46

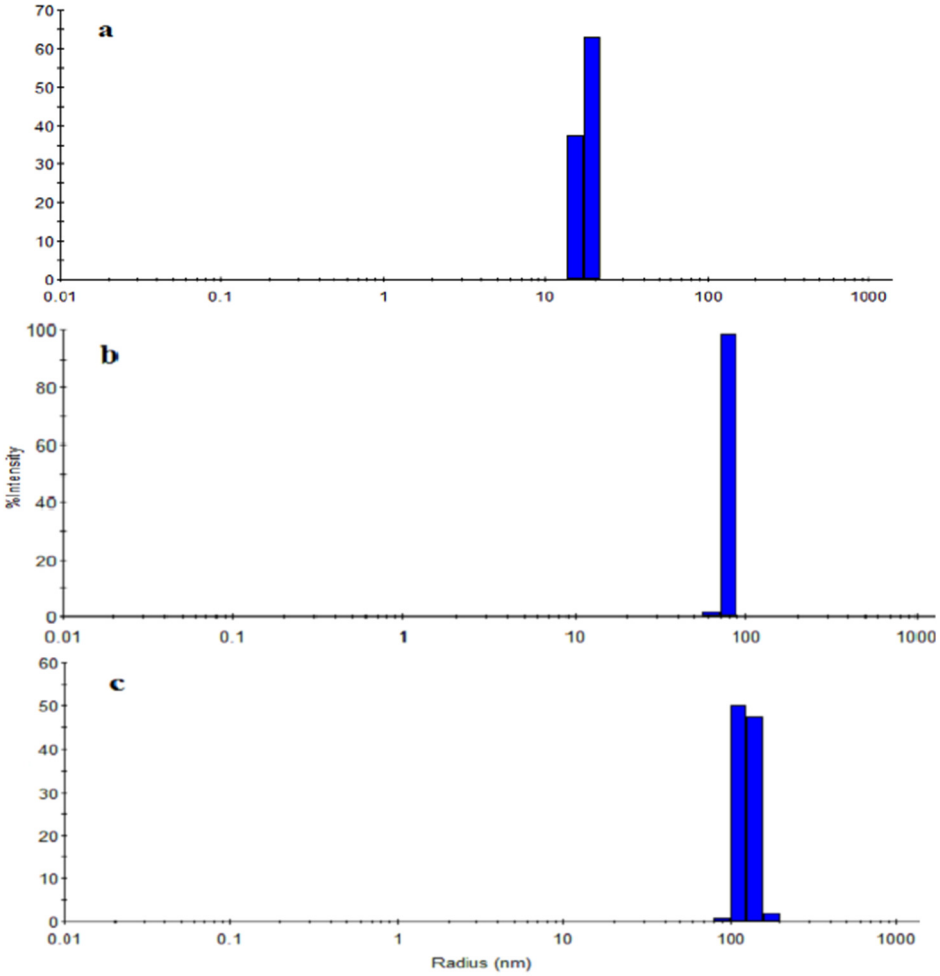


Figure 3. Particle size of (a) Fe_3O_4, (b) Fe_3O_4/SiO_2 and (c) Fe_3O_4/SiO_2-guanidine.

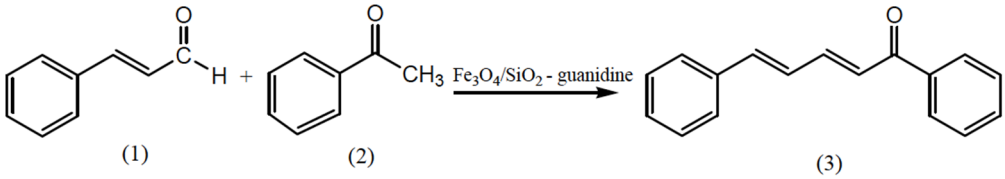


Figure 4. The reaction scheme for the synthesis of 1,5-diphenylpenta-2,4-dien-1-one.

aromatic and olefinic at 3023 and 3065 cm^{-1}, respectively. Furthemore, the peak at 1653 cm^{-1} and 1590 cm^{-1} showed the presence of C=O vibration and C=C groups, respectively. LC-MS spectrum showed the fragmentation at m/z 235 ($[M+H]^+$) and 257 ($[M+Na]^+$), confirming the formation of 1,5-diphenylpenta-2,4-dien-1-one (figure 5).

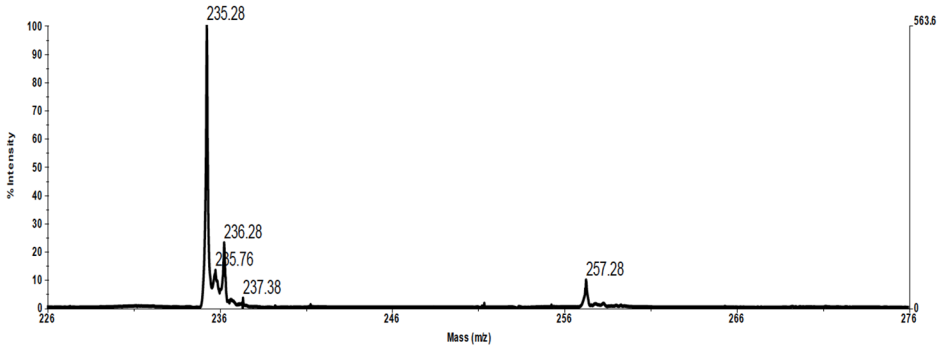


Figure 5. Mass spectrum of the 1,5-diphenylpenta-2,4-dien-1-one.

4. Conclusions

Fe_3O_4 nanoparticle was obtained by co-precipitation method using seaweed *Sargassum* Sp. as reducing agent and stabilizer. The characterization of Fe_3O_4 nanoparticle showed that silica coating and guanidine functionalization of the Fe_3O_4 was performed succesfully. The Fe_3O_4/SiO_2-guanidine organobase catalyst can be used in the synthesis of 1,5-diphenylpenta-2,4-dien-1-one compound by aldol condensation reaction between acetophenone and cinnamaldehyde. The UV-Vis, FTIR, and LC-MS spectrum confirmed that the 1,5-diphenylpenta-2,4-dien-1-one was succesfully synthesized.

Acknowledgements

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