The effect of polyethylene glycol addition on the synthesis of solid acid catalyst and its applications in esterification reaction

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Abstract. Synthesis of a catalyst by a sol-gel method is commonly conducted using a template to form pores to increase the number of active sites. In this work, mesoporous silica-carbon composites were prepared by sol-gel method using polyethylene glycol (PEG) 6000 as the template. Sodium silicate, commercially known as water glass, a cheap material, was used as the silica source. Here, PEG 6000 served as both the carbon source and the template. The silica-PEG composite was then carbonized at 550°C for 1 h to obtain silica-carbon composite. The sulfonate group was grafted into the composite by sulfonation with sulfuric acid at 100°C for 5 h. The sulfonated silica-carbon catalyst had a surface area of approximately 1490.8 m²/g. The very high surface area was able to hold a large amount of sulfonate group resulting an ion capacity of approximately 2.09. The composite was successfully used as heterogeneous catalyst for esterification of acetic acid with ethanol with a conversion of 90.27%, higher than that of commercially Flotrol F-007.

1. Introduction

Many methods have been used to synthesize solid catalysts, including precipitation and coprecipitation, sol-gel, and simple mixing (catalyst alloy) [1]. The sol-gel method seems to attractive from the viewpoint of the possibilities for manufacturers to design the catalysts according to their uses in the reaction. In addition, it also provides many possibilities to improve the internal structures and characteristics of the catalyst. The most common materials for use as the host are based on silica or alumina.

The sol-gel method has been long used to prepare porous materials for catalysts. For the case of silica-based catalyst, the commonly used silica precursor is based on alkoxides such as tetramethyl orthosilicate (TMOS) and tetraethyl orthosilicate (TEOS) [2]–[6]. However, the alkoxides are expensive and toxic that hinder for their commercial application. The initial stage of making this catalyst begins with making mesoporous silica composites, then impregnation is carried out to insert carbon in it, after which the desired functional groups are grafted according to the use of the catalyst in a reaction. Lu, et al, 2010 used hydroxyethylsulfonic acid to graft sulfonate groups on the silica-carbon composite mesopore to produce a solid acid catalyst for acetalization reaction [2]. Valley, et al, 2012, used 98% sulfonic acid to graft sulfonate groups on mesopore-silica-carbon composites (SBA-15, KID-6, and mesocellular silica) to produce solid acid catalysts for esterification reaction [4]. Especially for esterification reaction, this reaction requires acid catalyst, mainly solid acid catalyst.
which is easily separated from the reactant and product. Ion exchange resins is also used for esterification reaction [7]–[10], in addition to silica-carbon-based solid catalysts [4], [6], [11], and carbon-based solid catalysts [12]–[15].

In this paper, we propose to use an inexpensive sodium silicate as the silica source and PEG 6000 as the carbon source and template to prepare mesoporous silica-carbon composite. First, silica-PEG composite was prepared using a one-pot sol-gel synthesis from sodium silicate and PEG. The obtained composite was then calcined to convert PEG into carbon. The proposed method offers an advantage over the typical two-step route: (i) synthesis of mesoporous silica using template and (ii) impregnation the carbon source into the mesoporous silica. The use of one material with two functions would reduce the step of template removal and carbon source impregnation. This silica-carbon composite serves as a support for the solid catalyst. Furthermore, the performance of the catalyst is evaluated for esterification reaction of acetic acid with ethanol.

2. Materials and Methods

2.1 Materials

The materials used for the synthesis of catalyst were industrial grade sodium silicate solution (water glass; 28% SiO₂, SiO₂:Na₂O = 3.3) provided by PT. PQ Silica Indonesia, polyethylene glycol (PEG 6000; reagent grade, Merck), hydrochloride acid (HCl; 37%, Merck), sodium hydroxide (NaOH; Merck), sulfuric acid (H₂SO₄; 98%, Merck), and demineralized water. They were reagent grade and used as received without further purification.

2.2 Procedure

2.2.1. Preparation of silica-PEG composite. Silica-PEG composites were synthesized by following our developed procedure [16] with some modifications. Briefly, 30 mL of sodium silicate solution containing 8.0% of silica was added to 75 mL of acidic PEG 6000 solution (0,1; 0,25; 0,5, and 1 g of PEG 6000 in 30 ml of demineralized water and 45 ml of chloride acid 1 M) under stirring vigorously. The pH was adjusted to 4 by adding NaOH solution drop by drop under stirring. Then, it was degassed in a vacuum desicator to release gas bubble present in the solution, aged for 1 h at room temperature to form a gel, and dried in a freeze dryer for 48 h.

2.2.2. Preparation of silica-carbon composite. To produce silica-carbon composite, the silica-PEG composite was carbonized in a tubular furnace under flowing nitrogen gas at 550°C for 1 h.

2.2.3 Sulfonation of silica-carbon composite to produce catalyst. The catalyst was produced by sulfonation of silica-carbon composite using sulfuric acid under nitrogen atmosphere. One gram of the silica-carbon composite was dispersed in 25 mL 98% sulfuric acid. The mixture was heated at 100°C under constant stirring for 5 h. After heating, the mixture was diluted in demineralized water and cooled to room temperature. The solid was filtered from the mixture and washed with demineralized water to remove the residual sulfuric acid. The washing was finished when white precipitate could not be observed by adding BaCl₂. The solid sample was then dried with vacuum pump and stored in a desiccator for characterization.

2.2.4 Characterization. To determine of the characteristic of catalyst, the samples were analyzed by nitrogen adsorption-desorption at its boiling point using a gas adsorption-desorption instrument (Nova 1200, Quantachrome). The samples of catalyst were degassed at 300°C under flowing of nitrogen gas for 3 h prior to the measurement. The specific surface area was evaluated using the multi-point Brunauer-Emmet-Teller (BET) method at P/P₀ < 0.3. The average pore size was estimated from the desorption profile using the Barrett-Joyner-Halenda (BJH) model. The total pore volume was calculated at P/P₀ approached unity. The ionic capacity of the catalyst-samples was determined by acid-base titration method. The sample was immersed in 25 ml of 1 N NaOH solution for 48 h. The solid sample was filtered, and the filtrate was diluted 10 times with demineralized water and titrated with standardized 0.1 M HCl.
solution to determine the remaining NaOH concentration after immersion. The ionic capacity was then calculated by the number of moles of NaOH reacted with the sulfonate group divided by the initial mass of sample immersed.

2.2.5 Performance test of catalyst. To find out the performance, the catalysts was used for esterification reaction of acetic acid with ethanol in a three-neck flask under reflux. 40 mL of ethanol (99.9%, p.a., Merck) was reacted by 20 mL acetic acid (100%, glacial, Merck) with a loading catalyst of 0.2 g. The reaction was carried out for 3 h under constant stirring at 80°C. During reaction, 1 mL of aliquots was sampled from the reaction mixture for analysis. The acetic acid concentration in the aliquot was quantitatively analyzed using a gas chromatography (GC-model, Agilant 6890 series) equipped with a column (DB-WAX 122-7032, Agilent) and a flame ionization detector (FID). The column was operated at 12°C/min ramp from 35°C up to 240°C, kept for 5 min. The carrier gas was nitrogen with a flow rate of 2.5 mL/min and the volume of sample injected was 0.5 µL. The concentration of acetic acid was determined by external calibration and the reaction conversion was calculated by

$$X = \frac{C_{A0} - C_A}{C_{A0}} \times 100\%$$

(1)

where $C_{A0}$ and $C_A$ are, respectively, the initial and final concentrations of acetic acid. The same procedure was also conducted to Flotrol F-007, a commercial resin, as a comparison.

3. Result and Discussion
The preparation of catalyst started from the synthesis of silica-PEG composite as a basic material for catalyst support. Some amount of PEG 6000 (0.1, 0.25, 0.5, and 1 g) was added to 8% sodium silicate solution which was expected to serve both as a template to form pores in the silica-carbon composite and as a carbon source. One-pot synthesis in this case refers to the synthesis stage of silica-carbon composites and template removal was conducted simultaneously. The carbonization process was carried out under inert flowing nitrogen gas to release the volatile matters and to maintain the formed carbon adhering on silica surface. During the process, removal of the volatile matters left the previously occupied sites empty space to provide pores inside the silica-carbon composite. The formation of pores at this early stage is very important because it would significantly affect the characteristics of the catalyst including surface area and ionic capacity, and in turn, the overall catalyst performance.

The next process was the process of grafting sulfonate groups to porous silica-carbon composites to produce catalysts with the active sites of sulfonate groups that act as acid catalysts in the esterification reaction. This sulfonate group was grafted to silica-carbon composites using sulfuric acid reagents in the presence of atmospheric nitrogen. The presence of nitrogen serves to replace oxygen, so that oxidation was not occurring during the sulfonation process. The sulfonate group attaches to the silica-carbon composite with the van der Waals bond between carbon and sulfonate so that the sulfonate group will be able to exchange ions when used as a solid acid catalyst in the esterification reaction. An important parameter influencing the amount of sulfonate groups grafted on silica-carbon composites are the specific surface area of the material.

Variation of adding of PEG 6000 in the process of synthesis silica-PEG composites produce different pores in silica-carbon composites, as well as in the pores of the catalyst. The main effect of variations by adding of PEG 6000 is on the internal characteristics of the catalyst, such as pore size, pore volume, and specific surface area. Where these characteristics affect the performance of the catalyst in its application to the esterification reaction.
3.1 The effect of PEG 6000 addition to characteristic of catalyst

The addition of PEG 6000 at the synthesis of silica-carbon composites affects the characteristics of the catalyst, because PEG 6000 functions as a template and carbon source. The effect of PEG 6000 occurs mainly on the pore characteristics of the catalyst. This can be seen in Figure 2. Fig. 2 shows the effect of adding PEG 6000 to specific surface area, average pore size, and total pore volume on catalyst. Specific surface area, average pore size, and total pore volume ranged from 94.52 to 1490.76 m²/g, 2.72 to 4.27 nm, and 0.10 to 1.72 cc/g, respectively. Increasing the addition of PEG 6000 tends to increase the specific surface area, average pore size, and total pore volume of catalyst. But, there are the differences among the specific surface area and the total pore volume with the average pore size. The addition 0.5 g of PEG 6000 shows a decrease in the specific surface area and total pore volume of the catalyst, but an increase in the average pore size, which is 94.52 m²/g, 0.10 cc/g and 4.27 nm, respectively. This might be due to the addition of more PEG 6000 which no longer functions as a template, but instead wraps silica [17] which causes the inner pores to not form properly.

3.2 The effect of PEG 6000 addition to the ability of the catalyst to exchange ions and convert the esterification reaction

The addition of PEG 6000 tends to increase the specific surface area of the catalyst, where on the catalyst surface there is an active side of the catalyst, which is where the sulfonate groups attach to the catalyst. This sulfonate group plays a role in the reaction, in this case the esterification reaction. The ability of the sulfonate group as an ion exchange in this reaction was measured by ion capacity analysis. Meanwhile, the performance of the catalyst can be tested by involving the catalyst in the
esterification reaction between acetic acid and ethanol which is reacted at 80°C for 180 minutes. In this reaction, the conversion of acetic acid will be obtained which shows the performance of the catalyst in the reaction. The relationship between surface area, ionic capacity, and conversion of acetic acid in the reaction to the addition of PEG 6000 can be seen in Figure 3.

Figure 3 shows the effect of adding PEG 6000 to the catalyst surface area, the ionic capacity of the catalyst and the catalyst. Like the tendency for a specific catalyst surface area is the ionic capacity of the catalyst and the acetic acid conversion. Ionic capacity and reaction conversion are in the range of 0.98 to 2.09 and 2.75% to 90.27%, respectively. The figure shows that the specific surface area of the catalyst is proportional to the ionic capacity of the catalyst and the ability of the catalyst to convert acetic acid and ethanol in an esterification reaction. On addition 0.5 g of PEG 6000, the specific surface area of the catalyst decrease and this is followed by ionic capacity and catalyst conversion ability. This shows that the greater the specific surface area will allow the number of sulfonate groups grafted on the sulfonated catalyst so that the catalyst has a better ability to convert acetic acid and ethanol into ethyl acetate.

3.3 The comparison of catalyst performance with commercial resins
Commercial resins are frequently used by researchers as catalysts. For the esterification reaction, the type of resin used is usually cation exchange resin or also known as acid exchange resin. This is due to the presence of a sulfonate group in the resin which functions as an active group in ion exchange. Several types of resins used by researchers in the esterification reaction include amberlyst 15 [7]–[10], amberlyst 16 [10], amberlyst 131 [10], Indion 130 [9], Indion 190 [9], etc. To determine the performance of this catalyst in the esterification reaction, a comparison was made with the performance of a commercial resin, namely Flotrol F-007, and quantitatively it can be seen from the conversion of acetic acid which is converted to ethyl acetate when reacted with ethanol.

Figure 4. Performance of catalyst and Flotrol F-007 in esterification reaction at 80°C

Figure 4 shows the performance of the catalyst in the esterification reaction between acetic acid and ethanol at a temperature of 80 °C reaction temperature for 180 minutes using 0.2 g of catalyst prepared with the addition 1 g of PEG 6000 and by using a commercial resin, flotrol F-007. This figure shows that the equilibrium conversion occurs 60 minutes after the reaction begins and then tends to be almost fixed. The results of the reaction conversion using Flotrol F-007 were lower than the use of catalyst prepared with the addition 1 g of PEG 6000. At 60 minutes, the conversion achieved by Flotrol F-007 reached 57.46% and at 180 minutes it reached 63.66% while the catalyst with the addition of 1 gram of PEG 6000 reaching 90.27% for up to 180 minutes.
4. Conclusion
The addition of PEG 6000 in the initial step of the synthesis of catalyst, synthesis the silica-PEG composite, tends to increase the specific surface area to 1490.76 m$^2$/g and increase the catalyst ion capacity to 2.09. The catalyst was successfully converted acetic acid and ethanol with a conversion of 90.27% and higher than Flotrol F-007.

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