



The Use of Silica Extracted from Kaolin as Catalyst Support for Esterification of 4-Hydroxybenzoic Acid with Sucrose

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Abstract

SiO₂ was extracted from kaolin using concentrated HCl and HNO₃ mixture and used as solid support for both Bronsted (HClO₄ and H₂SO₄) and Lewis Acid (AlCl₃ and ZnCl₂). Before extraction, kaolin was calcined at 800°C for eight hours to form metastable kaolin. After the extraction procedure, silica was recovered in 51.6% yield. Silica and the resulting solid acids were then characterized using XRD, XRF, and FTIR. XRD pattern shows that silica synthesized from kaolin is in the mixture of amorphous and α-quartz silica. Immobilization of acids alters its structure becomes more crystalline. XRF analysis shows that the loading of AlCl₃ and ZnCl₂ was 9.5 and 24.8%, respectively. The acid catalysts were then used in the esterification reaction of 4-hydroxybenzoic acid with sucrose. The reactions were conducted in dimethyl sulfoxide (DMSO) solvent by varying reaction time and reaction temperature. The highest conversion of starting materials and selectivity towards ester was obtained over the AlCl₃/SiO₂ catalyst. DPPH radical scavenging test shows that the ester exhibits good antioxidant activity.

1. Introduction

Silica is a solid inorganic material with several unique characteristics, such as high surface area, high thermal stability, high absorption capacity, and ease of reactivation [1]. Therefore, silica is often used for various purposes such as adsorbent [1, 2, 3], catalyst or catalyst support [4, 5, 6], a hard template in the synthesis of porous materials [7, 8], and biomedical applications [9, 10]. One of the synthesis methods of silica is through extraction from aluminosilicate minerals such as kaolin [11] and bentonite [12]. Compared to the synthesis from silica precursors such as tetraethyl orthosilicate (TEOS), this method has some advantages, especially in terms of local natural resource utilization, which could reduce the synthesis cost and the dependency from an expensive precursor. Moreover, aluminosilicate mineral such as kaolin is an abundant mineral in Indonesia [13] and has high silica content, about 50% by weight [11].

Due to its acidity, silica is often used as an acid catalyst or catalyst support in some acid-catalyzed type reactions such as in esterification reaction [14]. In this case, Bronsted or Lewis Acid is immobilized on the silica surface to increase its acidity. The resulting acid

heterogeneous catalyst could then be used in the reaction. There are many reports on the utilization of heterogeneous acid catalyst in esterification reaction, such as Amberlit-IR120 [15], zeolite [16], zirconia [17], montmorillonite [17, 18], titanosilicate [19], heteropoly acids/carbon [20] or several mesoporous silicas synthesized from TEOS [21]. However, the utilization of silica, particularly extracted from kaolin as catalyst support for esterification reaction, remains unexplored. Therefore, herein we report our research on this issue. Esterification reaction between 4-hydroxybenzoic acid, a phenolic compound, and sucrose was selected as the reaction model since this reaction could produce an antioxidant, a substance with the ability to quench free radical. Previously, Farhoosh *et al.* [22] reported the antioxidative properties of some 4-hydroxybenzoic acid derivatives in the form of its ester, which are influenced by their structure. A recent study by Shim *et al.* [23] revealed that 4-hydroxybenzoic acid β-d-glucosyl ester extracted from *Pyracantha angustifolia* shows good antioxidant activity based on DPPH radical-scavenging test.

2. Methodology

2.1. Materials

All materials were used as received without any further purification. Kaolin was purchased from Bratachem; whereas HCl (37%), HNO₃ (70%), sucrose, 4-hydroxybenzoic acid (99%), dimethyl sulfoxide (99.9%), AlCl₃ (99%), ZnCl₂ (98%), HClO₄ (70%), H₂SO₄ (95–98%) were obtained from Sigma Aldrich.

2.2. Experiment

2.2.1. Extraction of Silica from Kaolin

Silica was extracted from kaolin according to the procedure reported by Bakri *et al.* [11]. Kaolin was calcined at 800°C for 6 hours to produce metastable kaolin. Then 15 mL of water, 280 mL of concentrated HCl, and 94 mL of concentrated HNO₃ (aqua regia) were added to 40.0 g of metastable kaolin. The mixture was stirred under reflux at 100°C for 8 hours in an air atmosphere condition. The resulting silica was filtered off, washed with acid-free distilled water, and dried in an oven at 110°C overnight.

2.2.2. Preparation of Silica Gel

A 30 g of extracted SiO₂ and 69 g of K₂CO₃ was mixed and crushed, and the mixture was melted in a furnace at 800°C for 3 hours. The resulting silicate was settled overnight and then soaked in 400 mL distilled water for 12 hours. The remaining precipitate was removed by paper filtration and washed with distilled water. A solution of 6.0 M HNO₃ was then added dropwise under stirring to the filtrate. Then it allowed standing for two nights at room temperature for the polymerization of silicic acid to silica hydrogel. The gel was filtered off and washed, then dried in an oven at 110°C overnight.

2.2.3. Acid Immobilization.

Immobilization of Bronsted Acids on silica gel was conducted according to the method reported by Chakraborti *et al.* [14] with some modifications. A 5 g of silica gel was dispersed in 10 mL of ether. Then 0.3676 g of concentrated HClO₄ (68%) was added, and the mixture was stirred for 30 minutes at room temperature. The solvent was then evaporated by air-drying, and the residue was dried at 110°C for 5 hours. The immobilization of H₂SO₄ was conducted using the same procedure to get acid loading of 5% (w/w). Whereas immobilization of Lewis Acids (AlCl₃ and ZnCl₂) was conducted via wet impregnation method, adopting the procedure reported by Bakri *et al.* [11]. A 3 g of silica gel was dispersed into 30 mL of 1 M AlCl₃ (or ZnCl₂) solution and stirred for 2 hours. Then the mixture was allowed to stand for 24 hours. The mixture was filtered, and the precipitate was dried in an oven at 110°C. The immobilization procedure was performed once for each acid, following the references as mentioned earlier.

2.2.4. Esterification reaction of 4-hydroxybenzoic acid with sucrose.

Esterification reactions were carried out by mixing 0.1380 g (1 mmole) 4-hydroxybenzoic acid, 1.0260 g (3 mmoles) sucrose, 10 mL dimethyl sulfoxide (DMSO), and 0.0400 g catalyst into a round bottom flask reactor

equipped with condenser and thermometer. The mixture was heated while stirring on a hotplate stirrer using a reflux system under an air atmosphere condition. The reactions were conducted by varying reaction temperatures (80, 100, and 120°C) and reaction times (0.5, 1, 2, 4, 8, and 24 h).

2.2.5. HPLC Analysis.

Separation and identification of products were performed with the HPLC instrument. The column used was a C₁₈ reversed-phase with a flow rate of 0.8 mL/min, column temperature of 40°C and injection volume of 20 µL. The gradient elution system was used according to the method proposed by Barbas *et al.* [24] for separating the parabens.

2.2.6. Antioxidant activity

The resulting product's antioxidant activity was determined using the DPPH• scavenging method [25, 26, 27]. A total of 2 mL of 0.2 mM DPPH solution was mixed in a vial with a 2 mL sample by varying sample concentrations from 10 to 75 ppm. The absorbance of the mixtures was measured at 515 nm every 5 minutes for a total of 30 minutes. The absorbance measurements were conducted once for each concentration to determine the product's inhibition concentration (IC₅₀). The same procedure was used to evaluate the IC₅₀ of ascorbic acid and 4-hydroxybenzoic acid as a comparison.

3. Results and Discussion

The extraction of silica from kaolin was conducted by using aqua regia. Prior to extraction, kaolin was calcined at 800°C for eight hours to form metastable kaolin. During this process, the dihydroxylation reaction occurred, causing a decrease in kaolin crystal volume and the Si-O-Al bond's strength. Thus, this thermal process facilitates the extraction of silica since the SiO-Al bond could be easily cleaved upon stirring in HCl-HNO₃ media. After the extraction procedure, silica was recovered in a 64.8% yield. To increase the surface area and pore volume, silica was further converted to silica gel [28]. Silica was reacted with carbonate to produce silicate, then polymerized in acidic conditions to produce the gel. The reactions are shown in Figure 1. After these processes, silica gel was recovered in 51.6%.

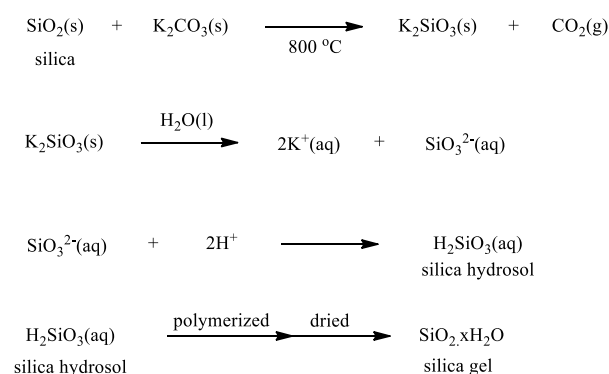


Figure 1. Reaction equations in the conversion of silica to silica gel

3.1. Catalysts Characterization

XRD data in Figure 2 shows that the silica gel synthesized from kaolin is in the mixture of amorphous and α -quartz silica. This is supported by the lack of sharpness (peaks) of the resulting diffraction pattern. Compared to the ICDD data, the structure of the synthesized silica gel is close to amorphous SiO_2 with the ID number of 82-1572 and α -quartz SiO_2 (ID 83-2187).

The synthesized silica gel was further used as catalyst support of HClO_4 and H_2SO_4 via acid immobilization method. The diffraction patterns of silica, kaolin, and the resulting $\text{HClO}_4/\text{SiO}_2$ and $\text{H}_2\text{SO}_4/\text{SiO}_2$ catalysts are shown in Figure 2. Based on XRD data, the diffraction patterns of the catalysts differ from that of silica gel, especially in the case of the $\text{H}_2\text{SO}_4/\text{SiO}_2$ catalyst. Sharp diffraction peaks appear at $2\theta = 23.5^\circ, 29.6^\circ, 33.9^\circ, 41.3^\circ,$ and 46.8° . This suggests that the immobilization of acid alter the structure of silica gel becomes more crystalline.

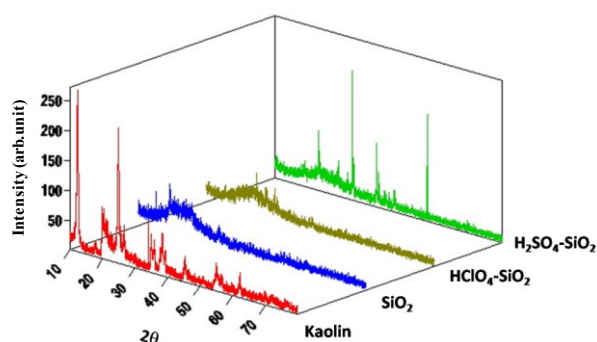


Figure 2. Comparison of diffraction patterns of kaolin, SiO_2 (silica gel), $\text{HClO}_4/\text{SiO}_2$, $\text{H}_2\text{SO}_4/\text{SiO}_2$

FTIR spectra of the support and catalysts are shown in Figure 3. In the spectra of silica, there is a wide band in the region between $3500 - 2800 \text{ cm}^{-1}$. This is a typical hydrogen bond of the $-\text{OH}$ group in a solid sample, which indicates strong hydrogen bonds, while the band at 1063 cm^{-1} shows the asymmetric vibration of Si-O-Si [29]. The band of Si-O-Si is also observed in the spectra of the $\text{HClO}_4/\text{SiO}_2$ and $\text{H}_2\text{SO}_4/\text{SiO}_2$ but shifted to a slightly longer wavenumber due to bond effect of the immobilized acid. In $\text{HClO}_4/\text{SiO}_2$, the band shifted to 1092 cm^{-1} , whereas in the $\text{H}_2\text{SO}_4/\text{SiO}_2$, it was shifted to 1096 cm^{-1} . In the spectra of $\text{H}_2\text{SO}_4/\text{SiO}_2$, there is also a sharp peak at 1383.95 cm^{-1} , which related to the asymmetric vibrations of O=S=O from the sulfate group. Whereas in $\text{HClO}_4/\text{SiO}_2$ spectra, there is a typical peak at 630 cm^{-1} , indicating the presence of HClO_4 in silica gel. The existence of this peak is also following what has been reported by Yang and Tang [30] regarding HClO_4 incorporation in nanoporous silica gels.

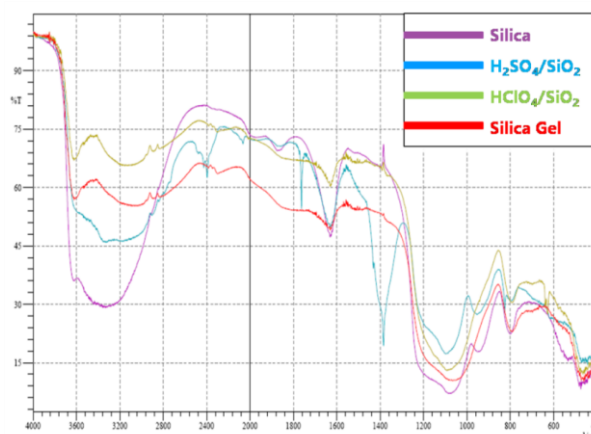


Figure 3. Combined FTIR spectra of silica, silica gel, $\text{HClO}_4/\text{SiO}_2$, and $\text{H}_2\text{SO}_4/\text{SiO}_2$ catalyst

Apart from being used as solid support for Bronsted Acids, the synthesized silica gel was also used as catalyst support for Lewis Acids, namely AlCl_3 and ZnCl_2 , via wet impregnation method. XRF analysis shows that the immobilization of Lewis Acids gave AlCl_3 and ZnCl_2 with acid loading of 9.5 and 24.8%, respectively, as shown in Table 1.

Table 1. Elemental analysis data of $\text{ZnCl}_2/\text{SiO}_2$ and $\text{AlCl}_3/\text{SiO}_2$ catalyst

$\text{ZnCl}_2/\text{SiO}_2$		$\text{AlCl}_3/\text{SiO}_2$	
element	%weight	element	%weight
Si	52.5648	Si	66.7275
Zn	24.8326	Al	9.5398
Cl	19.1464	Cl	17.1359
K	1.8198	K	4.3508

3.2. Esterification Reaction

Esterification of sucrose with 4-hydroxybenzoic acid produced pale yellow to brownish-yellow product mixture, as shown in Figure 4, depending on reaction conditions such as catalyst, time, and temperature. The longer the reaction time and the higher the reaction temperature tend to produce a darker colored reaction mixture. This indicates that more reactants were converted, and products were formed.



Figure 4. Typical appearance of the reaction mixtures obtained over the $\text{HClO}_4/\text{SiO}_2$ catalyst. (A) 80°C , 2 h; (B) 80°C , 4 h; (C) 80°C , 8 h; (D) 100°C , 8 h; (E) 120°C , 8 h.

HPLC analysis of all samples shows the same tendency, *i.e.*, the retention time of 4-hydroxybenzoic acid is higher than that of the forming esters. A typical

chromatogram of the sample is shown in Figure 5. In the chromatograph, 4-hydroxybenzoic acid has a retention time of 10.6 minutes while the esters have a retention time ranging from 4 to 6 minutes, which is shorter than that of the starting material. This suggests that the ester has higher polarity than 4-hydroxybenzoic acid due to the presence of several unreacted -OH groups from sucrose/glucose part of the ester. HPLC and MS data in Figure 6 suggest that the monoester dominates the products. This is related to the peak with m/z at 299 g/mol, representing the monoester of glucose/fructose.

3.2.1. Effect of acid type catalysts

Four catalysts gave almost the same conversion of 4-hydroxybenzoic acid (~70%), as shown in Figure 7, whereas selectivity of catalysts toward the formation of monoester varies from 87% for HClO₄/SiO₂ to 92% for AlCl₃/SiO₂. This highly selective but average in conversion

might be caused by the fact that the catalyst is lack of macroporosity character. The average pore diameter of the HClO₄/SiO₂ catalyst is only around 25 Å (classified as mesoporous material according to IUPAC nomenclature), with the surface area of 125 m²/g (Table 2). This could restrict the formation of di-, tri- or polyester of 4-hydroxybenzoate due to the size effect of those esters. Other catalysts could have similar textural properties since the support used was the same as that of the HClO₄/SiO₂ catalyst.

Table 2. Textural properties of HClO₄/SiO₂

Parameter	Value
Surface area (m ² /g)	125.01
Average of pore diameter (Å)	25.734
Total of pore volume (cc/g)	0.08043

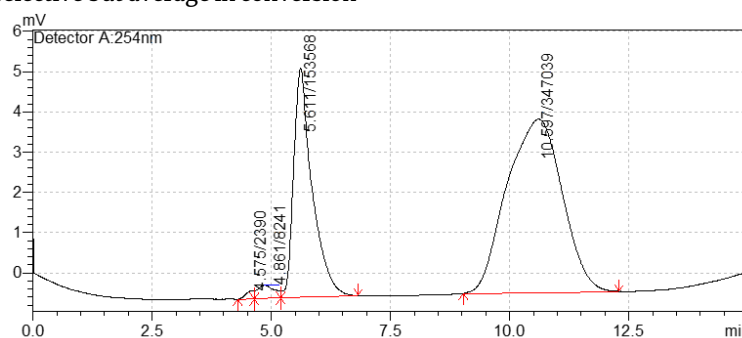


Figure 5. Typical chromatograph of the reaction mixture (reaction conditions: 1% of H₂SO₄/SiO₂ catalyst, 100°C for 4 hours)

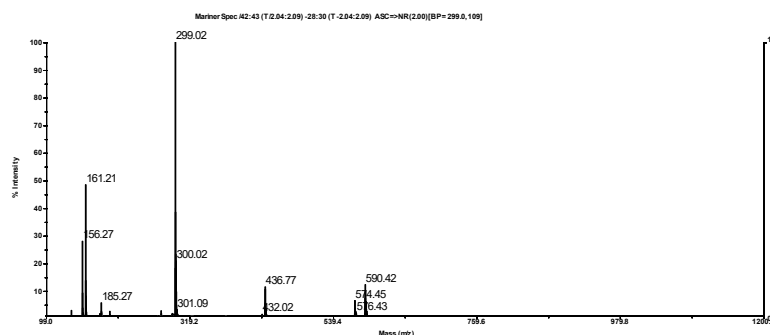


Figure 6. LC-MS of the ester

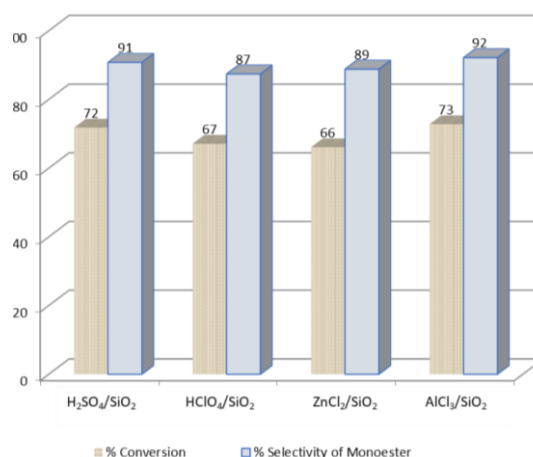


Figure 7. Activity and selectivity of various catalysts (reactions were carried out at 100°C for eight hours for all catalysts)

3.2.2. Effect of Reaction Time and Temperature

The higher percent of conversion was obtained in a longer reaction time since more reactants interact with each other, including the catalyst to form an ester. However, as shown in Figure 8(a), the reaction reaches equilibrium after 2 hours. This is due to the maximum catalyst activity, which is related to its lack of macroporosity character as described before. While for temperature effects, the data show that as the temperature rises, the percent of conversion also increases, which could be associated with the increasing of kinetic energy possessed by reactants. As shown in Figure 8(b), the reaction at 80°C gave only 4-hydroxybenzoic acid conversion of 42%, while an increase in reaction temperature up to 100°C increased the conversion to 65%. A further increase in temperature to 120°C only slightly increased the conversion to 71%.

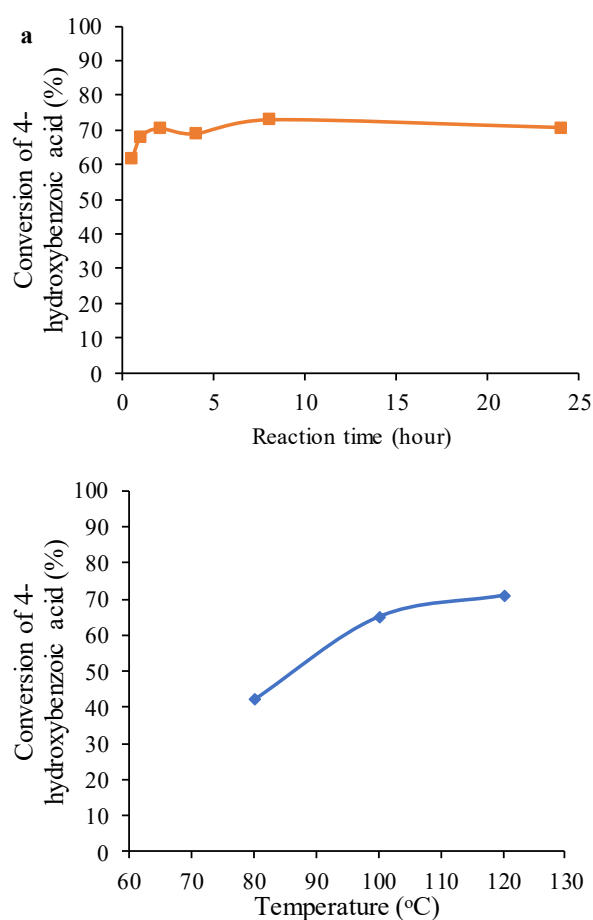


Figure 8. Effect of: (a) reaction time (over $\text{AlCl}_3/\text{SiO}_2$ catalyst) and (b) temperature to the 4-hydroxybenzoic acid conversion

3.3. Antioxidant activity of the Product

IC_{50} of the ester product was measured using the DPPH radical scavenging method, which gave the value of 65.07 ppm as a preliminary result. This means that the ester could quench 50% of free radicals at a concentration of 65.07 ppm. Thus, the ester shows a good antioxidant activity since the IC_{50} value is below 200 ppm [26]. The IC_{50} value of the ester is much lower than that of 4-hydroxybenzoic acid, and six times larger than that of

ascorbic acid, a commercially available and popular antioxidant (Table 3).

Table 3. Comparison of antioxidant activity of ester with 4-hydroxybenzoic acid and ascorbic acid. Radicals inhibition at 30 minutes

Ester		4-hydroxybenzoic acid		Ascorbic acid	
C (ppm)	% inhibition	C (ppm)	% inhibition	C (ppm)	% inhibition
10	15.45	1000	0.48	1	3.09
25	27.27	2000	2.55	10	54.74
50	41.82	3000	6.85	20	82.21
75	55.15	5000	12.58		
IC_{50}	65.07 ppm	17741.33 ppm		11.14 ppm	

4. Conclusion

Silica extracted from kaolin could be utilized as solid support for the immobilization of both Bronsted and Lewis Acid, and further used as a heterogeneous catalyst in esterification reaction of 4-hydroxybenzoic acid with sucrose. The high selectivity of the catalysts toward the formation of monoester might be caused primarily by the structure of the catalyst with its mesopore structure. The esters show good antioxidant activity with the inhibitor concentration (IC_{50}) of 65.07 ppm.

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