

FUNCTIONALIZATION OF SILICA FROM BAGASSE ASH WITH PRIMARY AMINES: FTIR ANALYSIS

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ABSTRACT

Organic silica from bagasse ash was successfully manufactured as a carbon dioxide gas adsorbent. Moreover, this is accomplished by functionalizing the silica surface's amine groups. Amines have high reactivity to CO₂ gas. Using the in-situ method, silanol groups can interact with amine groups. This research employs an in-situ technique in which the hydrolysis and condensation reactions co-occur to form a gel. Infrared spectroscopy was used to assess the efficacy of the functionalization of silanol and amine groups. This work aimed to examine the success of the functionalization of the amine group on the silica surface using infrared spectroscopy to produce carbon dioxide gas as an adsorbent. Fourier-Transform Infrared (FTIR) spectroscopy indicated a shift in silica groups produced by amine functionalization.

Keywords: Bagasse Ash, Silica Modification, Infrared Spectroscopy Analysis

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INTRODUCTION

Synthesis of organic silica from bagasse ash as the source of silica has been successfully conducted by managing gel-forming conditions. It is done by maintaining pH and using PEG (Polyethylene glycol) as a template.¹ This organic silica is prepared for a particular application, an adsorbent of gas CO₂. The specific characteristic needed here is silica with surface area, large pore sized, and is included in the mesoporous category. Other functional groups can replace quite a high silanol content on silica surfaces for occasional needs. For instance, is the modification of the silanol group with an amine group.²⁻⁴ Silica modified with amine groups is very potential for acid gas adsorb (CO₂ and H₂S) from natural gas or biogas.² As an adsorbent, silica is modified to add its adsorbing capacity.

The material characteristic that has been functionalized with an organic group can be done using Thermal Gravimetric Analysis (TGA), X-Ray Diffraction (XRD), Transmission electron microscopy (TEM) micrographs, or NMR Spectroscopic.⁵⁻⁶ In this analysis procedure, the sample in some temperature ranges is heated. The thermal evaluation of the selection is confirmed by the reading of the number on the infrared band. TGA analysis results give information on the interaction strength between an organic group that is modifying and the rising temperature treatment. TGA analysis's weakness is undetectable of changes caused by organic compound or water due to changing mass total created by *dehydroxylation* of silanol that happened on rising temperature.^{7,8} The problem occurs when a compound is decomposed at the same temperature and occurs in some temperature range.

This research uses the infrared spectroscopy (FTIR) analysis method. FTIR's analytical technique is more specific than TGDTA in detecting functional groups. Identification was carried out and confirmed by infrared absorption after heat treatment. This study aims to detect the success of modifying silanol groups with amine groups on silica gel from bagasse ash using the in-situ method with primary amine compounds.

EXPERIMENTAL

The raw materials for this study use bagasse ash from the sugar factory Kebon Agung in Malang, East Java,

Indonesia. The chemical substances were used directly, with no further processing. Sodium hydroxide (NaOH), hydrochloric acid (HCl), and sulfuric acid (H₂SO₄) from Merck, and as a modifying agent, 3-aminopropyl triethoxysilane was used (APTES) and ethanol (C₂H₅OH) as a solvent.

Synthesis of Silica-amine

The method of extracting silica on bagasse ash followed the previous procedure.⁹ 10 grams of bagasse ash was extracted with 60 mL of 2N NaOH solution and heated to its boiling point for one hour with constant stirring. Then cooled to room temperature and filtered with ash-free filter paper (Whatman No. 41). The filtrate is sodium silicate prepared as the main ingredient to produce silica.

Add APTS to sodium silicate from the extraction process of bagasse ash with NaOH solution. Previously, dissolved APTS in ethanol in a ratio of 1:1. Then 2N sulfuric acid was added to the mixture of APTS and sodium silicate slowly using a syringe pump with constant stirring of 1mL/min until it became a gel. Repeat this step with 2N hydrochloric acid. After that, the gel was aged for 18 hours at 40 degrees Celsius. Then the gel was washed with demineralized water many times and then dried for 24 hours at 100 degrees C.

FTIR Analysis

FTIR (Fourier Transform Infrared Spectroscopy) analysis is an analytical technique used to identify organics, polymers, and, in some cases, inorganic materials. FTIR analysis uses infrared rays to scan test samples and observe chemical properties. This analysis aimed to determine the presence of amine groups on the silica surface.

RESULTS AND DISCUSSION

Modification is mostly used in post-grafting, where the modification process is conducted when the silica gel has been formed. This method has some weaknesses i.e. porosity is reduced due to the attaching of the organic group to the pores' surface, and the amine charge level is limited, control of the level of loading rate and uniformity of the function group is challenging to achieve.⁹⁻¹² The research uses the in-situ method to resolve the post-grafting process's shortcomings as it is faster and more convenient.

In the in-situ process, surface modification co-occurs with gel formation. *Aminosilanes*, surfactants, and silica precursors are mixed, followed by an aging cycle to provide hydrolysis and condensation of the silica precursors.¹³ The mixing process between *aminosilane* and silica precursors requires a co-solvent because the silica precursor produced in this study is sodium silicate which uses water as a solvent. *Aminosilane* (APTS) used is insoluble in water. Therefore, a co-solvent is used, which can dissolve APTS and is entirely soluble in water. A suitable solvent is ethanol. After dissolving APTS in ethanol, it was mixed with sodium silicate to form a gel. The gel was allowed to stand for 18 hours, washed several times with ethanol and demineralized water, and dried. In reducing the synthesis steps, the in-situ method is more manageable than post-grafting and allows uniform distribution of functional groups without blocking the pores.^{9,14,15}

The success of silica gel modification with an amine group using the in-situ method was confirmed with spectra FTIR, as shown in Fig.-1. FTIR spectrum showed the changing of a functional group on a silica sample caused by amine group modification. Specific absorption bands for silica appeared in wave number 3743 cm⁻¹ (curve a), indicating a free silanol group on the silica surface. This absorption band was not shown on both curves anymore; it suggested that the amine group successfully exchanged silanol groups. Curves (b) and (c) showed a sharp peak in wave numbers 1410 cm⁻¹ and 1595 cm⁻¹ that showed amine firmly bound to the silica.⁴ The amine group's modification is also observed on absorption bands in wave number 3290 cm⁻¹, demonstrating stretch vibration from the -CH bond associated with the group -NH.

Infrared spectroscopy thermal analysis has superiority over thermal TGA analysis. It can be explained as follows: when the functionalization process of silica gel and amine group occurred, water and organic compounds were created that decomposed as a result of heat. With TGA, mass reduction caused by decomposition was shown as a total mass loss. Different from FTIR, that can differ two processes related to heat. Stretching tape of organic compounds was significantly differentiated from stretching band CH and O-H.

The addition of acids in the synthesis of silica-amines affects the catalysts involved in the gelling process. Both curves of silica samples made with hydrochloric acid and sulfuric acid show the same type. However, the curve of silica prepared with hydrochloric acid gives a sharper specific picture of amine silica than amine silica prepared with sulfuric acid. Sulfuric acid is classified as a strong acid because it has twice the

number of protons (H^+) as hydrochloric acid. The higher the proton concentration in sodium silicate, the more the silicate groups are protonated, so gel formation occurs faster. As a result, the amine compounds exchanged with silanol groups are smaller because polymerization and condensation have occurred.

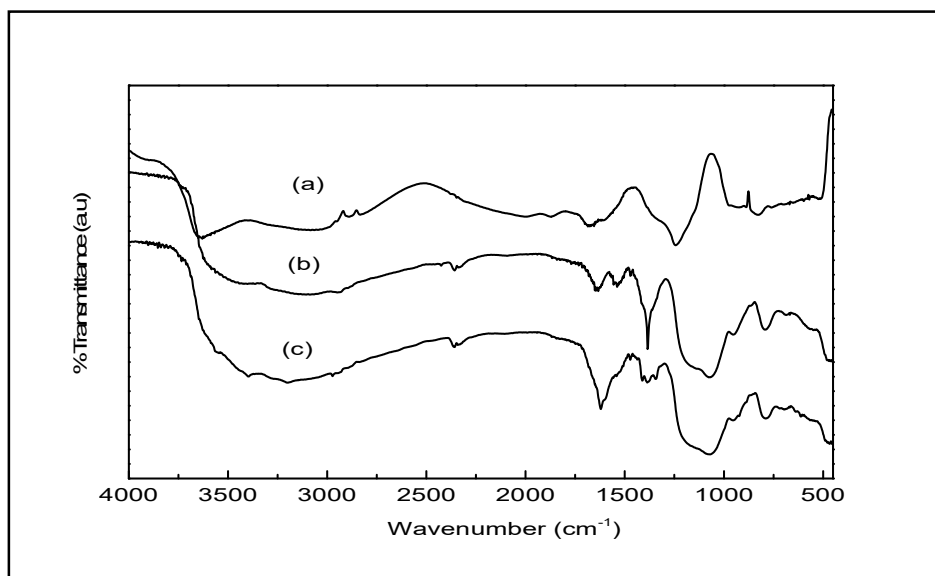


Fig.-1: Spectrum FTIR Sample (a) Pure Silica and Silica Prepared Using Acid (b) HCl; (c) H_2SO_4

CONCLUSION

The modification of silica gel with a primary amine compound was successful. A group of amines can exchange surfaces containing silanol groups on silica. Using FTIR, this modification is analyzed. Whereas the results of the FTIR analysis showed that silica-amine, prepared using hydrochloric acid or sulfuric acid, had specific peaks of silica amine on wave numbers 1410 cm^{-1} and 1595 cm^{-1} during the gel-forming process. It showed that amine was as firmly bound to silica. The FTIR curve of pure silica does not indicate absorption bands on the number of waves.

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