

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

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### ABSTRACT

Organic silica using bagasse ash as primary material was successfully produced as adsorbent carbon dioxide gas. This is achieved by substituting amine attribute groups on the silica surface. Amine is very susceptible to CO<sub>2</sub> emissions. Using post grafting and in-situ methods, Silanol groups can interact with amine groups. This work uses the in-situ approach, where hydraulic and condensation reactions are used in time to produce a gel. The effectiveness of functionalizing silanol and amine groups was analyzed using infrared spectroscopy. Fourier transform Infrared Spectroscopy analysis revealed a shift in a functional silica group induced by amine group alteration.

**Keywords:** bagasse ash, silica, functional group modification, an amine compound, infrared spectroscopy analysis

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### INTRODUCTION

Synthesis of mesoporous silica from bagasse ash as the source of silica has been successfully conducted by managing gel-forming conditions. This is done by maintaining pH and using PEG (Polyethylene glycol) as a template<sup>1</sup>. This mesoporous silica is prepared for a particular application, which is as adsorbent of gas CO<sub>2</sub>. The specific characteristic needed here is silica with surface area and large pore sized and is included in the mesoporous category. Other functional groups can replace quite a high silanol content on silica surface for occasional needs. For instance, is the modification of the silanol group with an amine group<sup>2,3,4</sup>. Silica modified with amine groups is very potential for acid gas adsorb (CO<sub>2</sub> and H<sub>2</sub>S) from natural gas or biogas<sup>2</sup>. As 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). In this analysis procedure, the sample in some temperature ranges is heated. The thermal evaluation of the sample is confirmed by the reading of the number on the infrared band. The result of TGA analysis gives information on the interaction strength between an organic group that is modifying and the rising temperature treatment. TGA analysis's weakness is undetectable of changing caused by organic compound or water as a result of mass changing total created by dehydroxylation of silanol that happened on rising temperature<sup>5,6</sup>. The problem occurs when there is compound decomposed at the same temperature and occurs in some temperature range.

This research uses an analysis method using infrared spectroscopy (FTIR). Analysis technique using FTIR is more specific in detecting a functional group. Identification is conducted and confirmed with infrared absorption after the heat treatment. This research is intended to change the silanol group with an

amine group on silica gel from bagasse ash by using the in-situ method with the compound of primary amine.

Modification mostly used is post-grafting, where the modification process is conducted when the silica gel has been formed. Conceptually, the grafting procedure can be considered a reaction between the hydroxyl group's surface and alkoxy ligands silane compound that caused the formation of the surface layer gathered with amine function. Thus, it can be assumed that all alkoxy ligands ideally will react with hydroxyl group surface to free suitable alcohol, that tend to  $(\text{SiO})_3\text{Si-R}$  forming. The advantage of the grafting method is the maintenance of the mesostructure after the modification process. Nevertheless, this method has some weaknesses. First, porosity is reducing due to the attaching of the organic group to the pores' surface and blocking because of the diffusion of the modifying agent into the pores<sup>7</sup>. Second, the amine charge level is limited due to the small number of silanol groups that can be exchanged because the condensation process has been run. To handle the post-grafting process's limitations, the in-situ approach is used as it is faster and more convenient. Fourth, control on the level of loading rate and uniformity of function group is challenging to achieve<sup>8,9</sup>. The in-situ approach was used to resolve the post-grafting process's shortcomings as it is faster and more convenient.

## **EXPERIMENTAL**

### **Materials**

The raw material used in this research was obtained from sugar cane factory Kebon Agung, Malang, East Java, Indonesia. The chemical substances were used directly without additional treatment. Those substances were obtained from Merck, which is sodium hydroxide (NaOH), hydrochloric acid (HCl), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) as a modifying agent used 3-aminopropyl triethoxysilane (APTES). Ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) is used as a solvent.

### **The Procedure of Synthesis of Silica-amine**

Sodium silicate from bagasse ash was obtained from the alkali extraction method<sup>10</sup>. 10gram of bagasse ash was extracted with 60 mL NaOH 2N solution and heated at its boiling point for one hour with constant stirring. It was then cooled at room temperature and filtered with paper filter ash-free (Whatman No. 41). The filtration was in the form of sodium silicate prepared as the primary material to make silica.

Sodium silicate resulted from the extraction process was added with APTS that has been dissolved in ethanol. Then, acid was inserted into the mixture slowly using a syringe pump with constant stirring 1mL/min until being a gel. After that, the gel was aging in 18 hours on 40-degree Celcius. Next, the gel was washed using demineralized water many times and then dried for 24 hours at temperature 100 degrees C.

## **RESULTS AND DISCUSSION**

In an in-situ process, the surface modification was performed with gel-forming. Aminosilane, surfactants, and silica precursors were combined, followed by the aging cycle to give Hydrolysis and precursors silica condensation<sup>11</sup>. The mixing process between aminosilane and silica precursor required co-solvent because the silica precursor produced in this study was sodium silicate that used water as a solvent. The aminosilane (APTS) used was not dissolved in water. Therefore, using a co-solvent that can dissolve APTS and dissolve properly in water. An appropriate solvent was ethanol. APTS was dissolved first in ethanol, then applied to sodium silicate until the gel was formed. The gel was aged, washed several times with ethanol and demineral water, and dried. In synthesis steps reduction, the in-situ method was more straightforward than post-grifting and permitted uniform distribution of functional group without blocking pores<sup>7,12,13</sup>.

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  $3743\text{ cm}^{-1}$  (curve a) that indicated a free silanol group on the silica surface. This absorption band was not shown on another both curves anymore; it indicated that the amine group successfully exchanged silanol groups. On curve (b) and (c), it showed a sharp peak in wave number  $1410\text{ cm}^{-1}$  and  $1595\text{ cm}^{-1}$  that showed amine firmly bound to the silica<sup>4</sup>. Amine group modification was also observed on the appearance of absorption bands in wave number  $3290\text{ cm}^{-1}$ , which showed stretch vibration from -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.

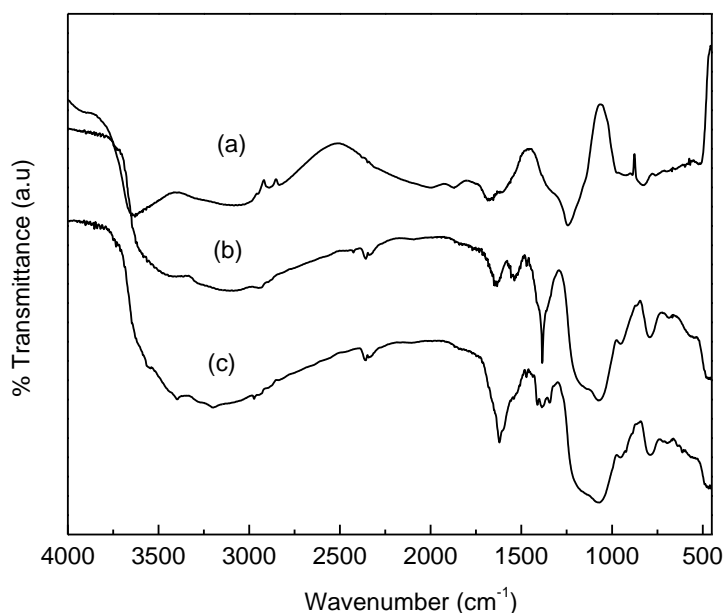


Figure 1. Spectrum FTIR sample (a) silica; and silica prepared using acid (b) HCl; (c) H<sub>2</sub>SO<sub>4</sub>

The use of acid on silica-amine synthesis gives impact as a catalyst on the gel-forming process. Both curves of silica samples prepared with hydrochloric acid and sulfuric acid showed a similar type. Nevertheless, the silica curve prepared with hydrochloric acid gave sharper specific peak of silica-amine than silica amine prepared with sulfuric acid. It occurred because sulfuric acid is strong acid two valences. The number of protons (H<sup>+</sup>) owned sulfuric acid is twice more prominent as hydrochloric acid belonging to strong acid monovalence. The higher concentration of proton in sodium silicate, the more perfect protonated the silicate group is so that the gel-forming happens faster. As a result, the amine compound that is exchanged silanol group is smaller because polymerization and condensation have been run.

## CONCLUSION

Modified silica gel with a primary amine compound was successfully carried out. A group of amines can exchange surfaces containing silanol groups on silica. Use 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  $1410\text{ cm}^{-1}$  and  $1595\text{ cm}^{-1}$  during the gel-forming process. This showed that amine was as firmly bound to silica. FTIR curve of pure silica does not indicate absorption bonds on the number of waves.

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### REFERENCES

1. N.A. Rahman, I. Widhiana, S.R. Juliastuti, H. Setyawan, Colloid and Surface A : Physicochemical and Engineering Aspect. 476, (2015), DOI: [10.1016/j.colsurfa.2015.03.018](https://doi.org/10.1016/j.colsurfa.2015.03.018)
2. H.Y. Huang, R.T. Yang, D. Chinn, C.L. Munson, Industrial Engineering Chemistry Research, 42 (2003), DOI: [10.1021/ie020440u](https://doi.org/10.1021/ie020440u)
3. G.P. Knowles, J.V.D. Graham, S.W. Delaney, A.L. Chaffee, Fuel Processing Technology, 86 (2005), DOI: [10.1016/j.fuproc.2005.01.014](https://doi.org/10.1016/j.fuproc.2005.01.014)
4. P.J.E. Harlick, A. Sayari, Industrial and Engineering Chemistry Research, 46, 2 (2007), DOI: [10.1021/ie060774+](https://doi.org/10.1021/ie060774+)
5. J.Y. Ying, J.B. Benziger, A. Navrotsky, Journal of the American Ceramic Society, 76, 10 (1993), DOI: [10.1111/j.1151-2916.1993.tb03983.x](https://doi.org/10.1111/j.1151-2916.1993.tb03983.x)
6. T.M.H. Costa, M.R. Gallas, E.V. Benvenuti, J.A.H. Jornada, Journal of Non-Crystalline Solids, 220, 2-3 (1997), DOI: [10.1016/S0022-3093\(97\)00236-6](https://doi.org/10.1016/S0022-3093(97)00236-6)
7. F. Hoffmann, M. Cornelius, J. Morell, M. Froba, Angewandte Chemie International Edition, 45, 20 (2006). DOI: [10.1002/anie.200503075](https://doi.org/10.1002/anie.200503075)
8. D.J. Macquarrie, , Journal Chemical Communications, 16 (1996), DOI: [10.1039/CC9960001961](https://doi.org/10.1039/CC9960001961)
9. M.H. Lim, A. Stein, Chemistry of Materials, 11, 11 (1999), DOI: [10.1021/cm990369r](https://doi.org/10.1021/cm990369r)
10. S. Affandi, H. Setyawan, S. Winardi, A. Purwanto, R. Balgis, Advanced. Powder Technology, 20 (2009), DOI: [10.1016/j.appt.2009.03.008](https://doi.org/10.1016/j.appt.2009.03.008)
11. S. Huh, J.W. Wiench, J.Yoo, M. Pruski, V.S.Y. Lin, Chemistry of Materials, 15, 22 (2003), DOI: [10.1021/cm0210041](https://doi.org/10.1021/cm0210041)
12. A. Sayari, S. Hamoudi, Chemistry of Materials, 13, 10 (2001), DOI: [10.1021/cm011039I](https://doi.org/10.1021/cm011039I)
13. X. Xu, C. Song, J.M. Andresen, B.G. Miller, A.W. Sacroni, Microporous and Mesoporous Material, 62, 1-2 (2003), DOI: [10.1016/S1387-1811\(03\)00388-3](https://doi.org/10.1016/S1387-1811(03)00388-3)