Silica Gel-Amine from Geothermal Sludge

S Muljani*, C Pujiastuti, P Wicaksono, R Lutfianingrum
Universitas Pembangunan Nasional ‘Veteran’ Jawa Timur
Rungkut Madya Gunung Anyar, Surabaya, Jawa Timur, Indonesia

*sriemuljani.tk@upnjatim.ac.id

Abstract. Silica Gel-Amine (SGA) has been made from geothermal sludge by grafting amine method. Sodium silicate solution is prepared by extracted geothermal sludge powder using sodium hidroxide solution then acidification in the range of pH 5 - 9 by using tartaric acid 1N. The grafting process uses 1 ml of ammonia solution and 10 ml of toluene at a rate of 0.1 ml min⁻¹ accompanied by a reflux process. The amine grafting is done in two methods. The first method is grafting amine in silicate solution and the second method is grafting amine in washed gel. Product SGA was confirmed by FTIR, TGA-DTG and BET characterization. The results show that the pH affects the amount of amine that is grafted onto silica gel. Differences in grafting method affect the size of the pore and surface area. SGA product prepared by grafting washed gel at pH 8 have pore diameter of 12.06 nm, surface area of 173.44 m²g⁻¹, and mass of decomposed amine compound 0.4 mg. In the presence of amine groups on the silica gel surface, these adsorbents may be able to selectively adsorb CO₂ gas from natural gas.

1. Introduction

The Silica gel is one of the chemicals in the form of solid which is widely used as an adsorbent. This is due to the ease of production and also some other advantages, namely: highly inert, hydrophilic, high thermal and mechanical stability and relatively unfold in organic solvents when compared to organic polymer resin solids. The quality associated with its utilization is determined by various factors, namely internal structure, particle size, porosity, surface area, resistance and polarity. The adsorptive properties are due to the presence of active sites on the silica surface.

Muljani et al [1] made silica gel from geothermal sludge by precipitation method using HCl and tartrate acid in the pH range of 5 to 9. The physical characteristics of silica using tartaric acid were much better than using HCl. The properties of silica gel are determined by the orientation of the ends in which the hydroxyl groups combine. Surface functionalization of inorganic fillers by an organic agent (modified agent) is usually an effective way to enhance the compatibility between organic and inorganic phases and even to form the covalent bonds between two phases to produce new characteristics [2]. The modification of silica gel is related to the process of changing the active site on the surface by changing the silanol group (=Si-OH) into another functional group which can generally be notated =Si-OM. In general, there are two ways to introduce amine into the solid supports. One is to graft amine groups on the support surface and the other is to load amines through impregnation. Three methods can be used for the grafting of amine: postsynthesis grafting, direct synthesis by co-condensation, and anionic template synthesis with the help of the interaction between the cation head in monoaminosilane and anionic surfactants [3]. Modifications can also coincide with controlling the structures, ie by the addition of a template compound. Mesoporous MCM-41, MCM-48 and SBA-15 were synthesized using Rice husk ash (RHA) as the silica source and their defective Si–OH sites were functionalized by 3-choroopropyltrimethoxysilane (CPTMS) which was subsequently...
grafted with amine compounds [4]. Synthesis of amine-grafted amino acid silica has been widely performed, Huang and Yang [5] successfully grafted MCM-41 silica gel using 3-aminopropyltriethoxysilan (APTS), which is selective against CO$_2$ and H$_2$S gases. The magnitude of the adsorption capacity is highly dependent on the amount of amine grafted on the silica surface. The characteristics of mesoporous silicas including MCM-41, SBA-15, and pore-expanded MCM-41 with pore size in a range of 2–17 nm, modified by mono-, di-, and tri-aminosilanes [6]. The porous silica gel-solid beads have been made from economically affordable water–glass precursors via sol–gel nano casting technique. A stable nanometric silica sol was prepared first from water glass and studied for surface potential and sol to gel transition [7]. SBA-15 prepared via ethanol extraction for template removing was grafted with three kinds of amine precursors (mono-, di-, tri-aminosilanes) to synthesis new CO$_2$ adsorbents [8]. The adsorption capacity of different amine-grafted samples was found to be influenced by not only the surface amine density, but also their physiochemical properties. The differences between the materials prepared via post-grafting amination vs traditional aminosilane grafting are attributed to the slightly increased spacing of the amines synthesized by amination because the alkylhalosilanes are initially better spaced on the silica surface after grafting, whereas the aminosilanes likely cluster to a greater extent when grafted on the silica surface [9]. Zhang [10] investigated a new synthesis procedure for colloidal dispersions of silica particles terminally grafted with polyethylene glycol (PEG) with a much improved stability in water as compared to known synthesis protocols. The procedure avoids any dry states or other circumstances leading to strong aggregation of the particles. The amine silica hybrid material supporting with precipitated silica processes relatively high amine content compared to three other amine silica hybrid prepared from fumed silica, MC-41, and silica gel [11]. In subsequent research the process of grafting amine in silica developed among others by nano-hybrid synthesis through immobilization of amine-functionalized silica gel nanoparticles with nanomagnetite via a co-precipitation technique [12].

The raw materials used as an amine source are usually 3-aminopropyltriethoxysilan (APTS) or polyethylenimine (PEI). Both materials are quite expensive and availability is also somewhat limited. This research used geothermal sludge as a source of silica with acidification process using tartaric acid and ammonia solution as source of amine compound. The purpose of this research is to develop grafting method (grafting) of amine group a) on silica gel and b) on silicate solution derived from geothermal sludge. The grafting method used in this research is co-condensation. This method has the advantage that the absence of a double reaction and it also requires little energy consumption, time and organic solvents.

2. Material and Method

Geothermal sludge (GS) in this work is obtained from the Geothermal Power Plant located in Dieng Wonosobo, Indonesia. GS in grinding up to about 100 mesh then washed using demineralized water. 500 gr of GS powder is put into beaker glass of 2000 ml, added demineralized water then stirred and then left to settle. After settling and then filtered using watchman paper. The washed GS is then dried in oven at 100 °C. The preparation of sodium silicate solution was done by mixing GS 10 gram with 200 ml NaOH 1N solution. The process of silica extraction at a temperature of about 100 °C with constant stirring for 1 hour. After that the solution is cooled to room temperature and filtered with watchman paper The sodium silicate solution was diluted with demineralized water at a ratio of 1: 2 and then added tartaric acid to achieve a pH adjusted at 5; 6; 7; 8; 9 respectively.

The amine-grafting process in the first method is prepared by addition of toluene to the gel formation process after the solution is achieve the adjusted pH 5-9. 1 ml of an ammonia solution was dissolved in 10 ml of toluene by injection at a rate of 0.5 ml min$^{-1}$. Furthermore, through the aging process for 24 hours. The gel was then washed with 100 ml of demineralized water three times and the filtered deposit was dried at 100 ° C. for 24 h.

The amine-grafting process in the second method is carried out after gel is formed at a pH adjusted in the range of 5-9, and after a 24-h aging process. The formed gel was washed using demineralized...
water as much as 100 ml. After washing process was added 1 ml of ammonia solution dissolved in 10 ml toluene by using syringe at the rate of 0.5 ml min\(^{-1}\). The obtained gel is filtered and then dried at 100 °C. for 24 h.

3. Result and Discussion

3.1 Effect of pH on the amine-grafted gel product.

Fig. 1 shows the effect of pH on the amine-grafted gel product. The resulting amine-grafted gel product increases at a pH increase of 5 to 7, but further decreases in the pH increase from 7 to 9. The amine-grafted gel product obtained from the amine grafting prepared in the silicate solution more than the amine-grafted gel product prepared after the silica gel was washed, this may be due to the following sodium tartrate during the transition process of solution from sol to gel.

Figure 1: Effect of pH on the amine-grafted gel product.

3.2 Effect of pH on FTIR characteristics of product Silica-Amine gel.

Figure 2a shows FTIR spectra for (a) gel product without grafting and (b) amine-grafted gel product. The FTIR spectra for silica gel products shows the presence of Si-OH silanol groups in the range 3600-3200, 1650-1550 and in the region of about 800 cm\(^{-1}\), but on the silica gel grafted amine there is a shift in the silanol group. This indicates the -OH group is replaced by the -NH group. The Si-O-Si group is present in the wavelength range 1100-1000 and 400 - 450 cm\(^{-1}\). The shift is characterized by a large tapered curvature, showing a stronger spectrum than silica without amine grafts, which tend to be loose (medium).

Figure 2a: FTIR spectra for (a) silica gel and (b) amine-grafted silica, pH 7

Figure 2b: FTIR spectra for (a) amine-grafted on silica gel (b) amine-grafted on silicate solution solution
Figure 3. Split IR spectra silica gel-amine prepared by grafting amine in silicate solution

Figure 4. Split IR spectra silica gel-amine prepared by grafting amine in washed gel

The strong Si-O-Si symmetric strain occurs at 1057-1060 cm⁻¹ while the medium asymmetric strain occurs in waves of about 447-436 cm⁻¹ as the pH increases from 5 to 9. For the group R-NH₂ primer, the medium N-H strain occurs at 3388-3397 cm⁻¹; medium buckling at 1636 cm⁻¹ and strong buckling at 788-793 cm⁻¹. Amine is decomposed in the temperature range of 300-400 °C where high energy is required to reduce the mass of silica gel, characterized by a sharp slope decrease on TGA. The results showed that the TGA profile had the sharpest slope decrease occurred in grafting amine at pH 8.

Figure 5. TGA for silica gel-amine produced from the second grafting method at a) pH 5, b) pH 6, c) pH 7, d) pH 8, e) pH 9
4. Conclusion
Silica Gel-Amine (SGA) has been made from geothermal sludge by two grafting amine method. The first grafting amine method at pH 8 is produced amine-grafted silica gel with a total pore volume of 0.7986 cm³ g⁻¹, an average pore diameter of 16.2041 nm and a BET surface area of 154.595 m² g⁻¹. The second grafting amine method obtained a total pore volume of 0.8625 cm³ g⁻¹, average pore diameter of 12.0663 nm, and the surface area of 173.442 m² g⁻¹.

Acknowledgment
We would like to thank the PT Geodipa Energi for providing the geothermal sludge. We also thank to the team of Material Research group, Chemical Engineering Department, UPN Veteran Jawa Timur.

References
[1] Muljani S, Setyawan H, Wibawa G, Altway A, 2014 A facile method for the production of high-surface-area mesoporous silica gels from geothermal sludge Adv PowTech 25 1593-1599
[2] Tung Lu H 2013 Synthesis and Characterization of AminoFunctionalized Silica Nanoparticles1, Colloid 75 311-318
[3] Ming BY, Lin BS,Yi Cao, Ying W, Zhu Ji W, Jian HZ, 2008 Efficient CO2 Capturer Derived from As Synthesized MCM-41 Modified with Amine, Chem. Eur. J., 14 3442–3451
[4] Bhagiyalakshmi M, Ji Yun L, Anuradha R, Tae Jang H 2010 Utilization of rice husk ash as silica source for the synthesis of mesoporous silicas and their application to CO2 adsorption through TREN/TEPA grafting J of Hazard Mater 175 928-938
[5] Huang HY and Yang RT 2003 Amine-Gratted MCM-48 and Silica Xerogel as Superior Sorbents for Acidic Gas Removal from Natural Gas Ind. Eng. Chem. Res., 42 12 2427–2433
[6] Chang FY, Tao KJ, Hsu-HC, Tan CS 2009 Adsorption of CO₂ onto amine-grafted mesoporous silicas Separ and Puri Tech 70 187-95
[7] Minju N, Abhilash P, Balagopal, Nair N, Mohamed AP, Ananthakumar S 2015 Amine impregnated porous silica gel sorbents synthesized from water–glass precursors for CO2 capturing. The ChemEngJ 269 · DOI: 10.1016/j.cej.2015.01.069
[8] Li Y, Sun N, Lei L, Zhao N, Xiao F, Wei Wei, Sun Y, Huang W 2013 Grafting of Amines on Ethanol-Extracted SBA-15 for CO₂ Adsorption Materials, 6 3 981-999
[9] Moschetta EG, Sakwa-Novak MA, Greenfield JL, Jones CW 2015 Post-Grafting Amination of Alkyl Halide-Functionalized silica for Applications in Catalysis, Adsorption, and 15N NMR Spectroscopy, Langmuir, 31 7 2218–2227
[10] Zhang Z, Berne AE, Willbold S, Buitenhouse J 2007 Synthesis of poly(ethylene glycol) (PEG)-grafted colloidal silica particles with improved stability in aqueous solvents J Col and Inter Sci 310 446–45
[11] Li KM, Jiang JG, Si-Cong T., Chen XJ, Yan F 2014 Influence of Silica Types on Synthesis and Performance of Amine-Silica Hybrid Materials Used for CO2 Capture J. Phys. Chem. C 118 5 2454–2462
[12] Elkady M, Hassan HS, Hashim A, 2016, Immobilization of Magnetic Nanoparticles onto Amine-Modified Nano-Silica Gel for Copper Ions Remediation, Materials 9 6 460.
[13] Belmabkhout Y and Sayari A 2009 Effect of pore expansion and amine functionalization of mesoporous silica on CO₂ adsorption over a wide range of conditions Adsorption, 15 3 318–328
[14] Rezaei F, Lively RP, Labbreche Y, Chen G, Y Fan Y, Koros WJ, Jones CW 2013 Aminosilane-grafted polymer/silica hollow fiber adsorbents for CO₂ capture from flue gas. ACS Appl Mater Interfaces 5 9 3921-31
[15] Choi S, Gray ML, Jones CW 2011 Amine-tethered solid adsorbents coupling high adsorption capacity and regenerability for CO\textsubscript{2} capture from ambient air ChemSusChem \textbf{4} 5 628-35