Study of Hydrogen Sulfide Adsorption on Silica Gel with Triethanolamine Layer

I Wayan Adi Suarya¹, Rachmat Triandi Tjahjanto^{1*}, Ulfa Andayani¹

¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, University of Brawijaya, Jl. Veteran 65145 Malang, Indonesia

*Corresponding e-mail: rachmat_t@ub.ac.id

Received 14 December 2021; Accepted 25 April 2022

ABSTRACT

Hydrogen sulfide (H₂S) is an impurity in gaseous fuels such as biogas, therefore this gas removal method is an interesting topic. The physisorption method is considered to be a simple work to be applied on a small scale. This research studies the impact of the addition of liquid triethanolamine on the porous silica on the adsorption of H₂S. The silica substrate is synthesized using two-pore templates namely a mixture of polyethylene glycol (PEG)/ sodium dodecyl sulfate (SDS) and the other one is pure chitosan. The silica surface was coated with triethanolamine (TEA) using the impregnation method. An H₂S gas adsorption study was conducted on the synthesized silica with and without TEA. The adsorption test was carried out by flowing H₂S from the reaction between FeS and HCl through the sample. The results of this study show that the TEA layer on the silica surface increases the adsorption towards H₂S gas, but it is relatively small compared to similar studies. The best result of combining TEA and silica gel is shown by TEA- sil-PS which was 3.8 x 10⁻⁵ mol H₂S per gram of adsorbent.

Keywords: physisorption, hydrogen sulfide, silica gel, triethanolamine.

INTRODUCTION

Hydrogen sulfide (H₂S) gas is an impurity in gaseous fuels that causes harm to humans and metal-based equipment. Natural gas and biogas can be used as safe fuels when the hydrogen sulfide gas content is removed or reduced to as low as possible. The presence of H₂S gas at low concentrations is known by the smell of rotten eggs, exposure to higher concentrations will cause can't to smell (olfactory fatigue), shortness of breath, and even death. The H₂S gas content in gas fuel will shorten the use-life of metal-based equipment. H₂S gas tends to be concentrated in the low ground because it has a molecular mass of 34.08 grams/moles or 19% heavier than air [1].

The physisorption method uses a substrate and a physical solvent to adsorb H_2S . Several previous studies reported the use of amine-based physical solvents (Table 1). The amount of adsorbed gas is fluctuating depending on the substrate and physical solvent.

The physical-based adsorption (physisorption) method was chosen for H_2S gas removal because it can reduce operational costs, can be regenerated, the process is simple, and can be applied to small biogas scales. The physisorption method uses a "physical solvent" that can interact with H_2S gas. Physical solvents such as monodiethanolamine (MDEA), polyethyleneimine (PEI), monoethanolamine (MEA), diethanolamine (DEA), hexamine, and triethanolamine (TEA) are some examples of amine-based physical solvents which are

The journal homepage www.jpacr.ub.ac.id p-ISSN : 2302 – 4690 | e-ISSN : 2541 – 0733

This is an open-access article distributed under the terms of the Creative Commons Attribution-NonCommercial 4.0 International which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. (http://creativecommons.org/licenses/by-nc/4.0/)

commonly used as acid gas adsorbents [3]-[5]. Triethanolamine has a tertiary amine functional group that can interact with H_2S gas and by some researchers is used for acid gas separation. This ability combined with silica gel which has advantages in the wide contact area is expected to be a synergy. Silica with a large surface area such as SBA-15 has been combined with TEA to adsorb H_2S gas of 0.1441 mg/gram adsorbent produced under pressure conditions of 0.4 MPa and TEA addition ratio of 23% [6]. Substrate silica has advantages in surface area synthesized with a PEG surfactant template with a molecular weight of 6000 g/mol and SDS and organic polymer in the form of chitosan as a pore-forming template. The use of PEG and SDS templates is expected to form pores with a micro-mesopore size range while chitosan organic polymers are expected to form pores with a meso-macropore range [7]-[9].

Physical solvent	Substrate	H ₂ S adsorbed (mg/g)	Ref
Polyethylene imine	Hierarchical pores structure silica monolith	43.18	[20]
Triethanolamine	Silica gel	0.19	[21]
Triethanolamine	Mesoporous silica SBA-15	0.1441	[6]
Hexamine	Mesoporous silica SBA-15	30.6	[22]

Table 1. Previous Study of H₂S Removal by Physisorption Method

EXPERIMENT

Chemicals and instrumentation

Chemicals and materials used in this work were sodium metasilicate Na₂SiO₃.9H₂O (*l*, Merck), polyethylene glycol (*s*, PEG 6000) purchased from DJ lab store (Malang), sodium dodecyl sulfate (*s*, Merck), chitosan from blue crab shell (*s*, *P. pelagicus*) 95,5% deacetylation degree purchased from Chimultiguna (Cirebon), acetic acid (*l*, Merck), triethanolamine (*l*, Merck), iron (II) sulfide with 99% purity (Pudak Scientific) (*s*), hydrochloric acid (HCl) \geq 37% (*aq*), CuSO₄.5H₂O \geq 98% purity (*s*), distilled water, and acetone (*l*, Merck).

Instruments used in this work for silica characterization were X-ray Diffraction (XRD) diffractometer type XPert MPD with Cu K α = 1.54060 Å. The functional groups were determined by Fourier Transform Infrared (FTIR) spectroscopy. Surface morphology and elemental analysis were characterized with Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX). Pores properties were characterized using nitrogen adsorption at 77 K using Brauner-Emmet-Teller (BET) method, Hovarth-Kawazoe (HK) method, Saito-Foley (SF) method, and Density Functional Theory (DFT).

Procedure

The silica gels were synthesized using the sol-gel method under acidic conditions using two types of templates. They were coded sil-PS for the silica gel synthesized using PEG and SDS templates, and sil-ch for the one synthesized using a chitosan template.

Preparation of sil-PS samples

The sil-PS samples were synthesized based on references [7],[8]. The polymer mixture template was prepared by adding 0.15 g of PEG and 0.83 g of SDS to 200 mL of acid acetate 2% (v/v). The solution was stirred using a magnetic stirrer for 30 minutes to obtain a homogeneous solution. Six grams of sodium metasilicate were added gradually to the template

solution. The mixture is covered with paper aluminum and aging at 60°C for 48 hours. Gel formed during aging and then separated from the solution by filtration with filter paper. Washing was carried out with 2% (v/v) acetic acid and continued with water distilled several times to remove the residue on the silica. The gel is dried in the oven at 80°C for 24 hours followed by calcination at 600°C for 24 hours four hours.

Preparation of sil-ch sample

The sil-ch samples were synthesized based on Witoon and Chareopanich [9]. The template was prepared by adding 1.5 grams of chitosan to the 60 mL 2% (v/v) acetic acid. Sodium metasilicate as the silica source was added as much as 4.5 grams gradually. The mixture was stirred using a magnetic stirrer accompanied by heating at 40°C for 30 minutes. The mixture was then covered with coated aluminum foil for aging at 60°C for 24 hours. The gel formed was then separated from the solution by filtering with filter paper. Washing was carried out with 2% (v/v) acetic acid and continued with distilled water several times to remove the residue on the silica. The gel was oven-dried at 80°C for 24 hours followed by calcination at 600°C for four hours.

Addition of a TEA layer on the sample's surface

The layer of TEA on the surface of the synthesized silica was carried out by the impregnation method. The amount of TEA used was 23% of the mass of silica dissolved in acetone. One gram of silica was added to the solution. The solution was then heated at a temperature of 50 °C for 24 hours until the acetone solvent evaporates and the TEA layer was expected to reach the silica surface [6].

*H*₂*S* gas adsorption test

The H₂S gas adsorption test on the sample was carried out as shown in Figure 1. The reaction occurred at the round bottom glass between FeS and HCl shown by number (2). Aerator (1) is used for pushing the resulting H₂S gas to pass through the sample in number (3). Residual gas H₂S which can pass through the hose is then captured as CuS by a 0.01 M CuSO₄ solution at the number (4). The data was obtained from the H₂S gas adsorption test in the form of blanks, silica samples with and without the TEA layer.



Figure 1. H₂S gas adsorption test scheme. Numbers and annotations: (1) Air pump as a booster (aerators); (2) Round-bottom flask; (3) Silicone hose with 60 cm length; (4) Erlenmeyer contains copper sulfate.

RESULT AND DISCUSSION

X-ray characterization performed on the silica samples showed an amorphous phase (figure 2). The powder diffraction patterns of sil-PS and sil-ch samples did not show a clear sharp peak and tend to widen around the 2θ angle between $20-25^{\circ}$ which explains the formation of amorphous silica [10].



Figure 2. XRD diffractograms of sil-PS and sil-ch

Infrared characterization was utilized to determine the functional groups present in the sample qualitatively (Figure 3). The FTIR spectra of the two silica samples showed identical results. Both sil-PS and sil-ch samples contain silanol groups as O-H vibrations at wavenumbers of 3481.38 and 3527.02 cm⁻¹ respectively wide and strong, as well as asymmetric strain vibrations (1108.17 and 1095.33 cm⁻¹) and symmetrical strain at 804.38 cm⁻¹ in both samples which is a characteristic of Si-O-Si bonds vibrating. Another peak that shows the silanol group is the vibration at the number 971.25 cm⁻¹ waves in sil-PS samples and overlapping in sil-ch samples. Group The detected function proves that the silica sample was successfully synthesized although it is also there are other groups detected as derivatives of carbon elements such as in the sample sil-PS with wavenumbers of 1645.85 and 1648.70 cm⁻¹ on sil-ch samples and 1511.78 cm⁻¹ which shows double and single carbon bonds [11]-[13]. The presence of the element carbon in the sample is possible from the rest of the template used to form the silica pore structure or condensation imperfect during the formation of silica gel.



Figure 3. FTIR Spectra of Silica Samples

SEM-EDX characterization shows surface morphology and elemental percentages of both silica samples (Figure 4). SEM photos show spots of the silica samples where the sil-PS sample particle size varies between $0.4 - 112 \mu m$ while that of the sil-ch sample varies from 5

- 180 µm. Visual assessment on the particle surface of the sil-PS sample so that it is smaller and rougher than that of the sil-ch sample. EDX spectra show the percentage of the elements carbon, oxygen, and silica. The average percentage of elements in the sil-PS sample are 34.73, 46.19, and 19.08, for C, O, and Si, respectively. Those values for the sample sil-ch are 16.20, 50.52, and 33.27. These data support the infrared spectra which suggest the presence of vibrations from the C-C and C=O bonds in the sample. In general, calcination at 600°C can reduce the amount of carbon in the sample, but because the calcination is carried out in a furnace in a stationary environment without gas flow, the carbon is not completely removed from the sample.



Figure 4. SEM Photos and EDX Spectra of sil-PS (1) and sil-ch (2)

Nitrogen gas adsorption on the sample (Figure 5) was carried out to determine the isotherm adsorption, pore volume, and surface area. Both sil-PS and sil-ch samples show a linear adsorption isotherm. The increase in the nitrogen adsorbed with pressure increase is directly proportional and constant without forming a hysteresis loop. This information suggests that both samples only had micro-sized pores (<2 nm) which support the absence of macropore size in the SEM photo above [14]. These results are unexpected, this study was aiming to obtain

porous silica with a range of pore sizes, such as micropores, mesopores, and macropores. The use of PEG and SDS, as well as chitosan as templates to form a pore, should be able to form porous material with a size bigger than micropores. The use of SDS surfactant as a template in other works forms micelles with diameters ranging from 3.5 to 4 nm [15]. Chitosan used as a template for the synthesis of sil-ch has a 95.22% degree of deacetylation which considerably good enough template to form hierarchical pores.



Figure 5. Adsorption isotherm of silica sample

Pore volume, pore diameter, and surface area of silica samples were compared based on HK, SF, and DFT methods (Table 1). HK method of calculating pore volume and pore size is based on nitrogen adsorption on the sample surface such as slits. The particles are calculated as pores while the SF method are based on gas adsorption nitrogen that fills the cylindrical micropores. Density functional theory (DFT) calculates the density of the sample as volume and size pore. The table shows the pore volumes of the two silica samples calculated based on the SF method is smaller than using the HK method which means the number of pores cylindrical shape that can be used as a "transport channel" in both samples is relatively small. Based on the difference in pore volume with the same pore diameter, it can be assumed that sil-PS samples have a higher number of pores. The surface area of sil-PS 451.4 m²/g is greater than that of the sil-ch 290.2 m²/g.

C	Pores volume (cm3/g)			Pores radius (Å)			Surface area
Samples	HK	SF	DFT	HK	SF	DFT	(m^{2}/g)
sil-PS	0.1796	0.1283	0.2065	3.676	4.522	16.136	451.4
sil-ch	0.1135	0.08187	0.1327	3.676	4.522	16.136	290.2

Table 2. Pore Volume, Pore Diameter, and Surface Area

 H_2S gas adsorption on the synthesized silica with or without the TEA layer (Table 2) overall shows a relatively small value compared to that reported by other reference journals. Calculations with a mass of 0.5 grams of FeS and 20 mL of HCl can be yields 5.6 x 10⁻³ moles of H_2S gas however, on measurements across a hose with a length of 60 cm in the absence of adsorbent was only detected at 7.9 x 10⁻⁴ mol or only 14% of the delivered H_2S . This value is the average of three repetitions which means uncontrolled factors of the hose against H_2S can

be assumed to be the same so that it can be compared. The following table shows the adsorption of H_2S gas on the selected adsorbent.

Sample Adsorption (moles/ gram adsorbent			
sil-PS	1.67 x 10 ⁻⁵		
sil-ch	6.28 x 10 ⁻⁶		
TEA- sil-PS	3.8 x 10 ⁻⁵		
TEA- sil-ch	8.4 x 10 ⁻⁶		

Table 3. Adsorption of H_2S on Synthesized Silica (with and without TEA Laye	r)
---	----

The adsorption of H_2S gas on the synthesized silica without a TEA layer shows that there are functional groups other than Si-O-Si which can capture H_2S gas. The functional group is detected in the FTIR spectra as C=C and in the EDX spectra, it was detected as the percentage of carbon elements thought to be derived from the template residue used. H_2S gas adsorption on silica samples that have been coated with TEA showed an increase in adsorption. This increase is due to the physical solvent of TEA that can interact with H_2S gas through its tertiary amine.



Figure 6. Suggested adsorption of H₂S on the sample with TEA coating according to the literature [2]

The adsorption test uses an aerator to help push the H₂S gas produced for 24 hours of reaction. The use of aerators causes free air components can also enter the sample including CO₂ gas from free air which also can interact with TEA. The presence of this gas may interfere with the test adsorption because based on the reference gaseous H₂S and CO₂ have equilibrium in TEA [16]. The interaction that occurs on the sample surface between the TEA layer with H₂S gas is suggested in Figure 6 according to the literature [2]. The results of this study are compared with the reference to calculate the reduction in surface area. The TEA coating on the reference sample decreases the surface area from 1,459 m²/g to 187 m²/g and increases the adsorption of H₂S gas by 1.07 mmol/g. Based on these results theoretically, the surface area of the silica sample after TEA coating in this study can be calculated. The change in sample surface area sil-PS silica after TEA coating is 451.4 m²/g which then becomes 6.64 m²/g or is reduced by 98.6% [17]. Decreased surface area is also reported by some references which use physical solvent coatings on porous materials with larger pore sizes. The percentage decrease in surface area due to the physical solvent is significant and fluctuates concerning the pore size range [18,19].

CONCLUSION

The TEA layer on the surface of the silica gel increases the adsorption of H_2S gas. Silica synthesized using PEG/SDS template and chitosan only showed pores in micro size. The largest surface area is shown by silica synthesized with PEG and SDS polymer mixture template which is 451.4 m² /g. The TEA coating on silica increases the adsorption of 2.13 x 10^{-5} moles of H_2S . The combination of TEA and silica gel is considered a poor H_2S adsorbent due to a small increase in the amount of the resulting adsorption.

REFERENCES

- [1] Strickland, J. US. EPA 2003, (CAS No. 7783-06-4)
- [2] Georgiadis, A. G., Charisiou, N. D., Goula, M. A. Catalysts, 2020, 10 (5), 521.
- [3] Bezerra, D. P., Oliveira, R. S., Vieira, R. S., Cavalcante, C. L., Azevedo, D. C. Springer Science, **2011**, 235–246.
- [4] Khabazipour, M., Anbia, M., *I&E Chem. Res.* 2019, 58, 22133–22164.
- [5] Okonkwo, C. N., Okolie, C., Sujan, A., Zhu, G., Jones, C. W., *Energy and Fuels* 2018, 32 (6), 6926–6933.
- [6] Chu, X., Cheng, Z., Zhao, Y., Xu, J., Zhong, H., Zhang, W., Lü, J., Zhou, S., Zhu, F., Zhou, Y., Zhou, L. Ind. Eng. Chem. Res. 2012, 51 (11), 4407–4413.
- [7] Singh, L. P., Bhattacharyya, S. K., Kumar, R., Mishra, G., Sharma, U., Singh, G., Ahalawat, S. Adv. Colloid Interface Sci. 2014, 214, 17–37.
- [8] Purwanto, A. S., Taslimah, T., Sriatun, S. J. Kim. Sains dan Apl. 2012, 15 (1), 1–6.
- [9] Witoon, T., Chareonpanich, M. *Mater. Lett.* **2012**, 81, 181–184.
- [10] Lalchhingpuii, Tiwari, D., Lalhmunsiama, Lee, S. M. Chem. Eng. J. 2017, 328, 434–444.
- [11] Handayani, P. A., Nurjana, E., Rengga, W. D. P. JBAT, 2015, 4 (2), 55–59.
- [12] Najafi, M., Yousefi, Y., Rafati, A. A. Sep. Purif. Technol. 2012, 85, 193–205.
- [13] Sari, L., Sudiarta, I. W., Putra, A.A.B. J. Kim, 2015, 9, 153–159.
- [14] Newalkar, B. L., Komarneni, S. J. Sol-Gel Sci. Technol. 2000, 18 (3), 191–198.
- [15] Hammouda, B. J. Res. Natl. Inst. Stand. Technol. 2013, 118, 151.
- [16] Fouad, W. A., Berrouk, A. S. *I&E Chem. Res.* 2012, 51, 6591–6597.
- [17] Zhang, H., Yang, C., Geng, Q., Fan, H., Wang, B., Wu, M. Appl. Surf. Sci. 2019, 497, 143815.
- [18] Han, Y., Hwang, G., Kim, H., Haznedaroglu, B. Z., Lee, B. Chem. Eng. J. 2015, 259, 653–662.
- [19] Shen, Z., Cai, Q., Yin, C., Xia, Q., Cheng, J., Li, X., Wang, Y. Chem. Eng. Sci. 2020, 217.
- [20] Chen, Q., Fan, F., Long, D., Liu, X., Liang, X., Qiao, W., Ling, L. *I&E Chem. Res.* 2010, 49, 11408–11414.
- [21] Zhong, L., Zhou, L. Front. Chem. Sci. Eng. 2011, 5 (3), 339–342.
- [22] Anbia, M., Babaei, M. IJE Trans. B, 2014, 11, 1697-1704.