



SELECTIVE ADSORPTION OF H₂S IN BIOGAS USING ZEOLITE PREPARED BY MICROWAVE-ASSISTED METHOD

Hoang Thi Thu Binh and Nguyen Quang Long

Faculty of Chemical Engineering, Ho Chi Minh City University of Technology, Vietnam

ARTICLE INFO

Received date: 25/01/2016

Accepted date: 08/07/2016

KEYWORDS

Biogas, H₂S, Zeolite X, microwave-assisted method, selective adsorption

ABSTRACT

This research focuses on development of a purification method for biogas - a potential sustainable fuel using Zn- exchanged zeolites. Different with traditional hydrothermal synthesis, the zeolite in this study has been synthesized via a microwave-assisted method in order to shorten the crystallization time. Various techniques were utilized for characterization of the adsorbents. The crystalline structure of the materials was analyzed by XRD (X-ray Diffraction). Scanning Electron Microscopy (SEM) was applied for morphology analysis. The H₂S adsorption activity of the material was determined by a fixed-bed absorption column and the expressed by the H₂S absorption capacity below a specified breakthrough point (50 ppm). H₂S adsorption capacity of about 13 mgS/g was achieved. It was observed that although high concentration of CO₂ was presented in the feed stream, the Zn-exchanged zeolite can selectively remove H₂S in the gas mixture.

Cited as: Binh, H.T.T. and Long, N.Q., 2016. Selective adsorption of H₂S in biogas using zeolite prepared by microwave-assisted method. Can Tho University Journal of Science. Special issue: Renewable Energy: 52-56.

1 INTRODUCTION

Biogas is one renewable energy source which generated by anaerobic degradation of organic substrates such as agricultural solid waste. In Viet Nam, until 2012 the number of biogas digesters with household size in the rural area is about 500.000 (Verbist *et al.*, 2013). The utilization of the biogas is limited because of the presence of H₂S in the gas, approximately 3%, which may lead to corrosion, catalyst deactivation and environmental issues (Bothi, 2007). Moreover, biogas contains large amount of CO₂, another acidic gas which compete with H₂S during the adsorption/absorption removal process. Therefore, it is important to selectively remove H₂S from biogas to expand the fuel application such as electricity generation or feed-

stock for chemical production via catalytic processes.

Desulfurization of the biogas stream can be done on various adsorbents such as metal oxides and zeolites (Kumar *et al.*, 2011; Allegue *et al.*, 2012). Curao (2010) reported that zeolites were widely used as adsorbents for removing different chemicals in a variety of processes, as shape-selective catalysts or supports for active metals in petrochemical industry and as ion exchangers. Most of studies on synthetic zeolite adsorbents for H₂S removal focused on ZSM-5, A and Y zeolites (Cosoli *et al.*, 2008; Sun *et al.*, 2015). By traditional hydrothermal synthesis method, it takes very long time, often some days, to obtain zeolites under 80 – 200°C (Cundy and Cox, 2003). Thus, for zeolite

synthesis, it is necessary to shorten the hydrothermal time to save energy and time.

This paper reports the application of home-used microwave oven for zeolite synthesis from cheap precursors which are available in Vietnam. The synthesized zeolite was characterized and tested for the selective removal of H₂S by an adsorption process.

2 METHOD

2.1 Zeolite preparation and characterization

The microwave equipment used in this study was a commercial microwave oven (EM-S6786V, Samsung, Korea) with 900 W output power at a frequency of 2.45 GHz. The oven was equipped with an electronic system in order to accurately control the temperature system. The control system provided pulsed microwave pumping by switching the magnetron, externally. Zeolite has been synthesized by mixture of silica, aluminum and sodium, which is prepared to anticipate forming: 4SiO₂:1Al₂O₃:6Na₂O:250H₂O. Liquid glass was used as silica sol (40 wt %) and aluminum hydroxyl was used as aluminum source (AR, 66.67%) and the presence of excess sodium solution (AR, 99.9%). Initially, an amount of sodium hydroxide, silicon source and distilled water was mixed and then stirred at room temperature. At the same time, aluminum hydroxide was dissolved slowly in sodium solution until the solution was clarified. Both mixture was mixed together by stirring with higher speed and then was aged at room temperature for 24 hours. After that, the mixture was transferred into a glass bottle then put in microwave oven system with attached to a condenser. Temperature was controlled during this period by irradiating to a constant temperature of 100°C for 45 – 180 minutes under microwave power. At the end, the product was centrifuged many times using deionized water until neutrality and the resulting solid product was dried at room temperature. (Bukhari *et al.*, 2015)

In the next step, the zeolites were ion-exchanged at 70°C for 4 hours with 0.5 M Zn²⁺ aqueous solution, the total volume of Zn²⁺ solution was used fivefold excess amounts to that required in order to ensure the completed ion-exchange. Then, the mixture was washed with distilled water in order to completely remove the unreacted Zn²⁺. The Zn-exchanged zeolites were collected after dried at 100°C overnight. The collected solid was pulverized and mixed with 10% bentonite by a mixer for 1 hour with a speed of 200 rpm. Afterwards they

were extruded to particles with the same size (2 mm diameter and 5 mm length). Finally, the pellets were calcined at 500°C for 4 hours in a static oven.

The zeolite was characterized by several bulk and surface analysis techniques including scanning electron microscope (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.2 H₂S removal test

The adsorption system consists of gas cylinders from commerce for production of H₂S/N₂ and H₂S/N₂/CO₂ model mixtures. The adsorbent was packed in a Pyrex U-tube reactor (diameter 0.8 cm and height 25 cm) which located in a temperature controllable furnace. H₂S concentrations were measured continuously by a H₂S sensor system purchased from Alphasense, England and be calibrated by Gastec H₂S-test kit (Japan). All the experiments were carried out at room temperature (30 ± 2°C), atmospheric pressure. The H₂S adsorption capacity of the material was calculated by the following equation:

$$C_s = 10^{-3} \times \frac{M_s}{m_{\text{sorbent}}} \frac{F \cdot P}{R \cdot T} \int_0^{t_b} (C_{s\text{in}} - C_{s\text{out}}) dt \quad (1)$$

Where: C_s - H₂S adsorption capacity (mgS/g); M_s - molecular weight of S (= 32); m_{sorbent} - mass of the adsorbent; C_{Sin} - H₂S concentration of the input stream; C_{Sout} - H₂S concentration of the output stream; F - total gas flow rate; t_b - time of the adsorption until the concentration of the output stream higher than the breakthrough point (breakthrough time).

3 RESULTS AND DISCUSSION

Samples were compared with XRD pattern of pure Zeolite X and specific peaks of Zeolite X were obtained. It can be seen from Figure 1a that the first weak peaks appeared on the XRD pattern after 1.5 hours hydrothermal microwave time. The intensity and sharpness of the diffraction peaks were significantly enhanced and continued with increasing time. The zeolite X was acquired after 2 hours. When it grew up to 3 hours, there were the presence of diffraction pattern of alpha crystalline quartz corresponding to the diffraction peaks after 2θ = 45° (Treacy and Higgin, 2007). The effect of the irradiation source power can also be realized. As observed from Figure 1b, using higher source power at constant time, not only makes the crystal growth faster but also increases the intensity and

sharpness of the diffraction peaks. Higher power will give smaller penetration depths and speed up

crystallization so that crystal can be formed with less time (Gharibeh *et al.*, 2009).

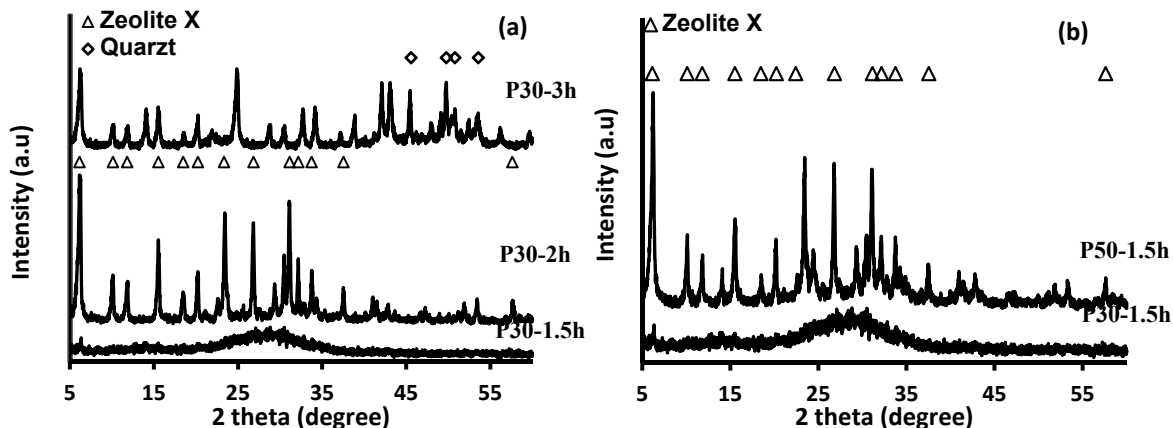


Fig. 1: XRD pattern of samples (a) synthesized at various microwave treatment times
(b) synthesized at various microwave powers

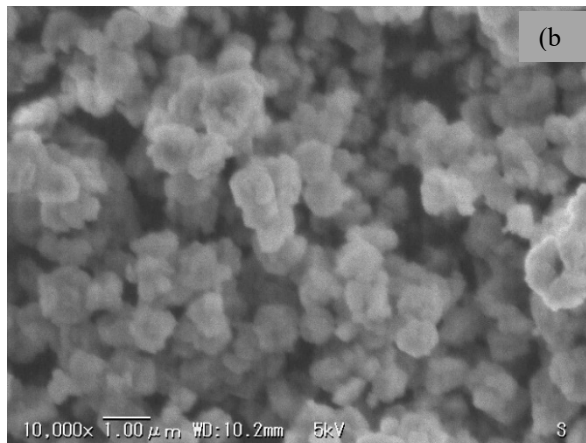
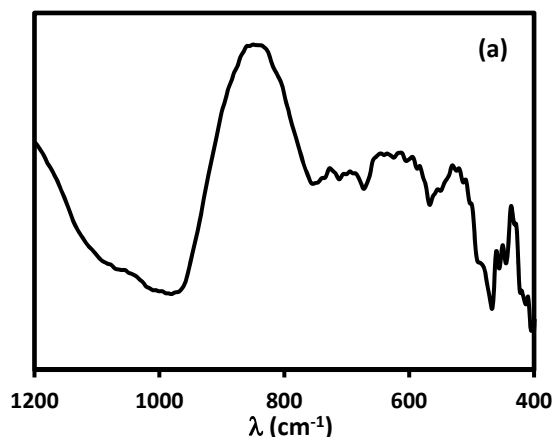


Fig. 2: (a) FTIR spectra of sample ZP30 -2h (b) SEM images of sample ZP30 -2h

The mid-infrared region ($1200 - 400 \text{ cm}^{-1}$) of spectra is informative characterization of the framework of zeolite. In Figure 2a, the main asymmetric stretch is at 970 cm^{-1} . The symmetric stretches occur at 752 and 672 cm^{-1} . The band at $548 - 566 \text{ cm}^{-1}$ is associated with the double 6 rings that connected to the sodalite cages. And a TO_4 bending vibration

occurs at 480 cm^{-1} . Furthermore, the morphology of zeolite samples are presented through SEM images (Figure 2b), it showed that the synthesized zeolite crystals were relatively uniform in sizes which were smaller than $1 \mu\text{m}$. This results are consistent with the publication by Bandura *et al.* (2013) and Franus *et al.* (2014).

Table 1: The specific surface area of NaX zeolites and ICP results

Sample	Microwave heating time (h)	S_{BET} (m^2/g)	ICP Results
ZP30 - 2h	2	159.06	1.82
ZP30 - 3h	3	229.07	1.73
ZP50 - 1.5h	1.5	122.81	1.54

Furthermore, to determine the specific area and the ratio of Si/Al, the BET method and ICP analysis were performed and the results are presented in Table 1. The surface areas from 122 to $229 \text{ m}^2/\text{g}$

were achieved. Increasing crystallization time caused to enhancing crystallinity and crystal size of zeolites. For 1.5 hours crystallization time due to low crystallinity, the specific surface area has the

lowest and increasing time to 2 hours, the specific surface area reaches $159 \text{ m}^2/\text{g}$. Low crystallinity will reduce the specific surface area due to the fact that the amorphous aluminosilicate will block outside pores of the zeolite crystals (Yates and Chem, 1968). Moreover, a further increase in the crystalli-

zation time leads to the growth of crystals to become larger particles leading to the decrease of the specific surface area. The ICP result indicates that the Si/Al ratios of the sample arrange from 1.5 to 1.8 and it is suitable for the zeolite X (Xu *et al.*, 2009).

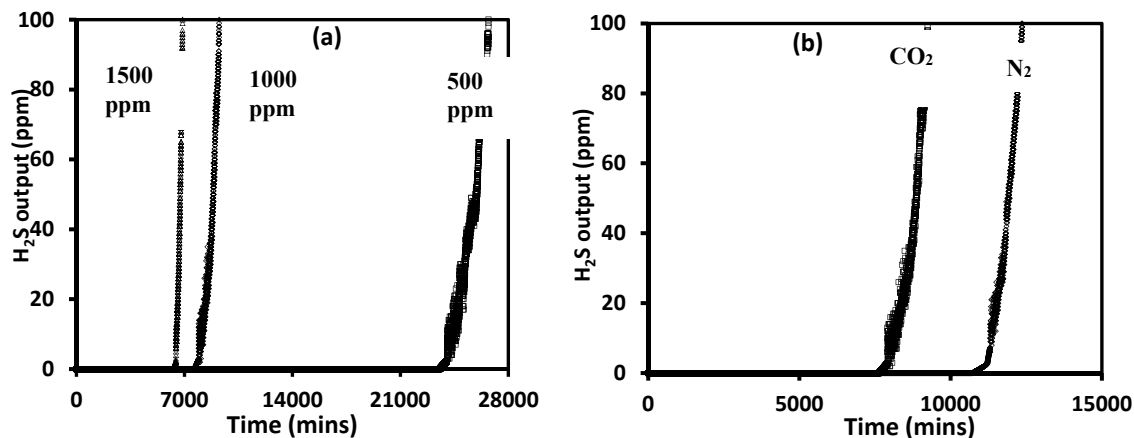


Fig. 3: Effect of (a) H₂S concentration (b) presence of CO₂ on the H₂S removal activity of sample ZP30 – 2h

To examine the hydrogen sulfide removal activity, the absorption experiments were carried out until the H₂S concentration of the outlet stream was recorded at about 100 ppm. The Figure 3a indicates the influence of the initial H₂S concentration against adsorption process. At lower initial H₂S concentration (500 ppm), the zeolite ZnX could adsorb H₂S in the feed-stream for about 7.5 hours and it was reduced to 1.7 hours at the initial H₂S concentration of 1500 ppm. Calculation, material (1 g) can adsorb H₂S at 9.5 g so with the average biogas production 3.5 m³/day of biogas digester in Vietnam household, 15 g zeolite are required, it

can be potential to economic problem. Furthermore, it is also known CO₂ may present up to 35% volume of biogas (Allegue *et al.*, 2012) so the presence of CO₂ in feed-stream may affect the H₂S treatment activity of the material. As seen from the Figure 3b, despite of high concentration of CO₂, which was more than 30 times higher than the concentration of H₂S, the ZnX still can selectively adsorb H₂S. Table 2 summarizes the H₂S capacity value of Zeolite X. The capacity of 13.8 mgS/g was attained without CO₂ at 1000 ppm H₂S feed-stream and it was decreased to 10.2 mgS/g when 40000 ppm CO₂ presence in the gas mixture.

Table 2: H₂S adsorption data for the ZnX- based sorbent at 1000 ppm H₂S feed-stream

Process parameters	Adsorption mass, m (g)			
	0.5	1.0	1.5	1.5
CO ₂ concentration (ppm)	0	0	0	40000
*H ₂ S adsorption capacity (mgS/g)	8.1	11.6	13.8	10.2

* Capacity values were calculated with breakthrough point is 50 ppm

4 CONCLUSIONS

The zeolite type X was successfully synthesized by the microwave heating technique and the effects of heating microwave time and the level of microwave power on the characteristics of zeolite were investigated. The results showed that after 1.5 hours or 2 hours which was depended on the microwave heating power, the zeolite's crystalline was generated. The desulfurization potential of

material was tested and maximum desulfurization capacity of material of 13.8 mgS/g was observed. Due to the selectively H₂S adsorption, the adsorbent is suitable for removal of H₂S from biogas which contain excess CO₂.

ACKNOWLEDGEMENTS

The authors would like to thank the Department of Science and Technology – Ho Chi Minh city (No. 76/2015/HĐ-SKHCHN) for supporting this research.

REFERENCES

- Allegue, L.B., Hinge, J. and Allé, K., 2012. Biogas and bio-syngas upgrading, Danish Technological Institute: 5-97.
- Bandura, L., Franus, W., Panek, R., Wdowin, M., 2013. Synthesis of zeolites from fly ashes—the industrial scale. *Global Journal on Advances Pure and Applied Sciences*. 1: 574-579.
- Bothi, K.L., 2007. Characterization of biogas from anaerobically digested dairy waste for energy use. Cornell University: 1-99.
- Bukhari, S.S., Behin, J., Kazemian, H., Rohani, S., 2015. Synthesis of zeolite NA-A using single mode microwave irradiation at atmospheric pressure: The effect of microwave power. *The Canadian Journal of Chemical Engineering*. 93(6): 1081-1090.
- Cosoli, P., Ferrone, M., Pricl, S., Fermeglia, M., 2008. Hydrogen sulphide removal from biogas by zeolite adsorption: Part I. GCMC molecular simulations. *Chemical Engineering Journal*, 145(1): 86-92.
- Cundy, C.S., Cox, P.A., 2003. The hydrothermal synthesis of zeolites: history and development from the earliest days to the present time. *Chemical Reviews*. 103(3): 663-702.
- Currao, A., 2010, *Understanding Zeolite Frameworks*, University of Bern: 1-65.
- Franus, W., Wdowin, M., Franus, M., 2014. Synthesis and characterization of zeolites prepared from industrial fly ash. *Environmental monitoring and assessment*. 186(9): 5721-5729.
- Gharibeh, M., Tompsett, G.A., Yngvesson, K.S., Conner, W.C., 2009. Microwave synthesis of zeolites: effect of power delivery. *The Journal of Physical Chemistry B*. 113(26): 8930-8940.
- Kumar, P., Sung, C.Y., Muraza, O., Cococcioni, M., Al Hashimi, S., McCormick, A., Tsapatsis, M., 2011. H₂S adsorption by Ag and Cu ion exchanged faujasites. *Microporous and Mesoporous Materials*. 146(1): 127-133.
- Sun, Y., Han, S., 2015. Diffusion of N₂, O₂, H₂S and SO₂ in MFI and 4A zeolites by molecular dynamics simulations. *Molecular Simulation*. 41: 1095-1109.
- Treacy, M.M. and Higgins, J.B., 2007. *Collection of simulated XRD powder patterns for zeolites fifth (5th) revised edition*. Elsevier.
- Verbist, V., Ton, D., Phlix, G., 2013. Mid-term Evaluation SNV programme 2007–2015 In-depth study of the Vietnamese Biogas Programme.
- Xu, R., Pang, W., Yu, J., Huo, Q., Chen, J., 2009. *Chemistry of zeolites and related porous materials: synthesis and structure*: John Wiley & Sons.
- Yates, D.J.C., 1968. Studies on the surface area of zeolites, as determined by physical adsorption and X-ray crystallography. *Canadian Journal of Chemistry*. 46(10): 1695-1701.