THE COMPARISON OF CARBON DIOXIDE AND HYDROGEN SULFIDE ADSORPTION USING ACTIVATED CARBON, CHEMICAL VAPOR DEPOSITION ON ACTIVATED CARBON AND ZEOLITE

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ABSTRACT

In this work, the Granular Activated Carbon and Zeolite A was applied for carbon dioxide and Hydrogen Sulfide removal. The adsorbents were characterized by scanning electron microscope (SEM), X-Ray Diffraction (XRD) and Nitrogen adsorption/desorption (BET). The improvement of adsorption capacity is using 30%W/W polyethyleneimine (PEI) and 1 mol/dm^3 of $LiNO_3$. Granular Activated Carbon was deposition with acetylene and impregnated with 30%W/W polyethyleneimine (PEI) and compared with the impregnated by 1 mol/dm^3 of $LiNO_3$. The adsorbents (GAC, PEI/CVD/GAC, Li/CVD/GAC, Zeolite5A, Li/Zeolite 5A and PEI/Zeolite 5A) were tested by using the synthetic biogas (45% CO_2, 10% N_2, 45% CH_4.and 105 mg/dm^3 of H_2S). The performance of carbon dioxide and hydrogen sulfide adsorption results have showed that PEI/CVD Activated Carbon is the good adsorbent for the low concentration of H_2S and Li/5A is the good adsorbent for CO_2 adsorption. The purity of the outlet methane was 81.53, 98.1, 96.6, 80, 93.16, 80.6 and 98.3% for zeolite 5A, Li/5A, PEI/5A, GAC, Li/CVD/GAC and PEI/CVD/GAC, respectively. The selectivity in the H_2S/CH_4 ratio of GAC is higher than zeolite 5A. The selectivity of the CO_2/CH_4 ratio of Li/5A is higher than GAC. Finally, the maximum adsorption capacity of the PEI/CMS (PEI/CVD/GAC) samples was 3.86 m mol CO_2 /g adsorbent, respectively.

Keywords: Activated carbon, carbon dioxide adsorption, hydrogen sulfide adsorption, polyethyleneimine chemical vapor deposition granular activated carbon, zeolite A.

INTRODUCTION

Biogas is produced from anaerobic degradation of organic material. It is a mixture composed of approximately 50-70% CH_4, 30-50% CO_2 and smaller amounts of NH_3 (80-100ppm), H_2S (500-1,000 ppm) and hydrocarbon (<100 ppm) [1]. The biogas advantage can be used directly to generate electricity and heat energy. The disadvantage of using gas engine is the reduce recovery of the energy content in the biogas. The biogas purification up to natural gas grade for its use as natural gas substitute for car fuel. Purification to remove CO_2 and H_2S is required. Hydrogen Sulfide corrodes vital mechanical components within engine generator and vehicle engines if it is no removed. When burning H_2S, it will be converted to SO_2 which is one of the pollutants. H_2S is the bad smell in wastewater treatment plant, animal processing and the food processing plant. [2]

The method to remove CO_2 and H_2S, amine aqueous solution absorption has been in industrial method for CO_2 and H_2S, removal for decades. However, amine absorption is unfit for H_2S removal in case of low concentration due to loss of solution, corrosive and expensive. [3, 4]. Activated Carbon are used for carbon dioxide adsorbents because of low cost and high thermal stability. Carbon molecular sieve (CMS), which are the narrow pore size distribution of activated carbon. Zhang et. al. study the adsorption capacity of 2.27 mmol/g of activated carbon at 298 K. Nowadays, the amine or high oxidizing agent impregnated on adsorbent will be increase the rate of adsorption. The improvement of the CO_2 adsorption, such as PEI impregnation and chemical vapor deposition process to develop the adsorption capacity of granular activated carbon. Rewadee et.al. study the preparation of CVD/ GAC from coffee bean which is the good adsorbent for CO_2 removal by using synthetic biogas (30% CO_2, 20% N_2 and 50% CH_4. [5]

Zeolite has played a major role in the development of adsorption technology. Zeolite are porous crystalline aluminosilicate. The framework consists of an assemblage of aluminate and silicate tetrahedral, shared oxygen atoms to form an open crystal lattice. Zeolite Molecular sieve are widely used as sorbent for gas separation due to large surface area. Zeolite 5A has the carbon dioxide adsorption capacity of 4.73 mg/g at 298K. [6]. Therefore, Zeolite 5A has been proved for H_2S removal. Song et.al. [7] produced the nanoporous composite sorbent called "molecular basket' by loading polyethyleneimine (PEI) on molecular sieve such as MCM41 and SBA15. Yang et all [8] produce the strong oxidizing ability, transition metal of Zn [9], Cu[10] and Fe[11] have been studied for H_2S adsorption and oxidation.

The main objective of this work is to prepare the GAC, CMS (CVD/GAC), CMS (Li/CVD/GAC), CMS (PEI/CVD/GAC), Zeolite 5A, Li-Zeolite 5A and PEI Zeolite5A, respectively were investigated its CO_2 and H_2S removal performance.

EXPERIMENTAL

Preparation for adsorbents

Commercial granular activated carbon (GAC) was purchased from METRA Co. Ltd. It was dried at 200 °C for 2 hours. Seventy grams of the CMS which prepared by Chemical vapor deposition on Granular Activated Carbon (CVD/GAC) was deposited with acetylene by chemical vapor deposition process under 15 ml/min of acetylene and followed with 50 ml/min of nitrogen flow at 800 °C for 30 min. Polyethyleneimine (PEI) was dissolved in ethanol and impregnated with CVD/GAC in the ratio of 30%W/W. (PEI/CVD/ GAC). It was dried at 105 °C overnight. The obtained product is PEI/CVD/GAC. Zeolite 5A was purchased from Takeda Co. Ltd. It was dried at 200 °C for 2 hours. PEI/Zeolite 5A was

prepared by dissolution of Polyethyleneimine in ethanol solution. Zeolite 5A was impregnated with PEI solution in the ratio of 30%W/W. It was dried at 105 °C overnight. Li/Zeolite 5A was prepared by impregnation 1M $LiNO_3$ on zeolite A for 30 min in the ration of 30% W/W. The obtained products were washing to remove the soluble impurities off and calcinations in order to remove volatile compounds. The final product was dried at 105°C overnight and keep in the desicators as shown in Table1.

Table 1. Activated method studied.

Materials	Activated method
1.Zeolite 5A	Drying in oven at 200°C for 2h.
2. Li- 5A zeolite	Drying in oven at 200°C for 2h.
3. PEI/Zeolite A	Drying in oven at 105°C for overnight.
4. Granulated Activated Carbon (GAC)	Drying in oven at 200°C for 2h.
5. PEI/CVD/GAC	Deposited with acetylene by chemical vapor deposition process under 15 ml/min of acetylene 30 ml/min of N_2 gas flow at 800 °C for 30 min followed impregnated with PEI (30%W/W) and drying at 105°C for overnight
6. Li- CVD/GAC	Deposited with acetylene by chemical vapor deposition process under 15 ml/min of acetylene 30 ml/min of N_2 gas flow at 800 °C for 30 min followed impregnated with 1M of $LiNO_3$ and drying at 105°C for overnight

Characterization of Samples

Scanning Electron Microscope (SEM) analysis was carried out by using JSM-6400. (JEOL, Japan). X-Ray Diffraction (XRD) was performed using Cu-Kα radiation (Rigaku Corp., Japan). The analysis of specific surface area, pore volume, and pore size were determined by nitrogen adsorption-desorption isotherms at 77 K with discontinuous volumetric apparatus (Quantachrome AUTOSORB 1).

Adsorption Experiments

The sorption tests were carried out using a SS-304 tube with the inner diameter of 3 cm and height of 100 cm. in which 70 grams of the various adsorbent was packed. (GAC, PEI/CVD/GAC, Li/CVD/GAD, Zeolite 5A, PEI/Zeolite 5A and Li/Zeolite A). A synthetic biogas (45% CO_2, 10% N_2, 45% CH_4.and 105 mg/dm^3 H_2S) was passed through the sorbent at the flow rate of 0.1 lit/min at the room temperature. The outlet of CO_2 and H_2S concentration was detected by a biogas 5000 analyzer. The adsorption equipment was shown in Figure 1.

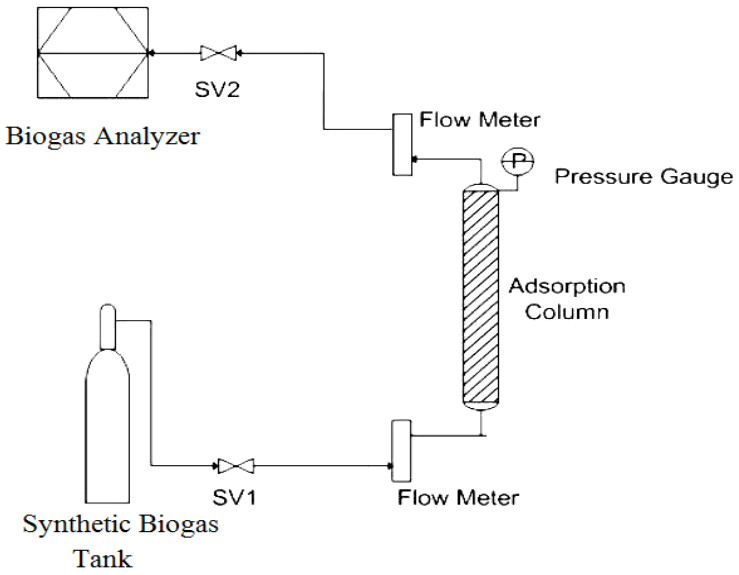

Figure 1. Diagram of the single column system.

The breakthrough concentration of CO_2 and H_2S was defined as 50% and 10%, respectively of the initial concentration. The test was stopped when the CO_2 and H_2S concentration outlet reaches the breakthrough set point. The removal efficiency can be calculated by using the eq.1.

The Removal Efficiency (H_2S and CO_2) = (C_0-C_e) x 100/C_0 (1)
where C_0 is the initial of CO_2 and H_2S concentration.C_e is the outlet of CO_2 and H_2S concentration.
The selectivity of CO_2/CH_4 can carried out by calculating the outlet gas of CO_2/CH_4 by using equation (2). and (3).
The Selectivity = mol outlet of CO_2/mol outlet of CH_4 (2)
mol (n_e) = PeV_e/RT (3)
where T is the temperature (K), R is the gas constant of 0.082 (dm^3atm/mol K), P is the pressure in operating condition.(atm)
Ve is the gas volume (dm^3). The condition was under given flow rate, initial concentration and mass of the various sorbent.

RESULTS AND DISCUSSION

Characterization of Adsorbent.

The Scanning Electron Microscope (SEM) image of the GAC, CMS_{GAC} (PEI/CVD/GAC), Zeolite 5A and Li/Zeolite 5A as shown in Figure 2. GAC and CMS $_{GAC}$ (PEI/CVD/GAC) have a rough shape but zeolite 5A and Li/Zeolite 5A has a cubic shape and size of 2-3 um as shown in Figure.2 c-d. SEM technique was applied in order to study surface morphology of adsorbents. The Figure. 2 shows that the porous surface of CMS_{GAC} (PEI/CVD/GAC) has more micropore than GAC.

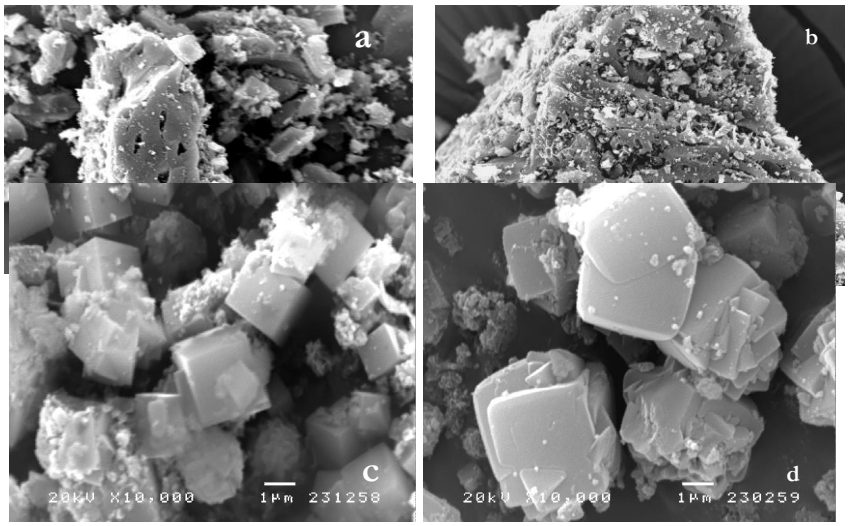

Figure 2. SEM images of (a) GAC, (b) CMS_{GAC} (PEI/CVD/GAC), (c) zeolite 5A and Li-5A zeolite.

3.2 Adsorption performance

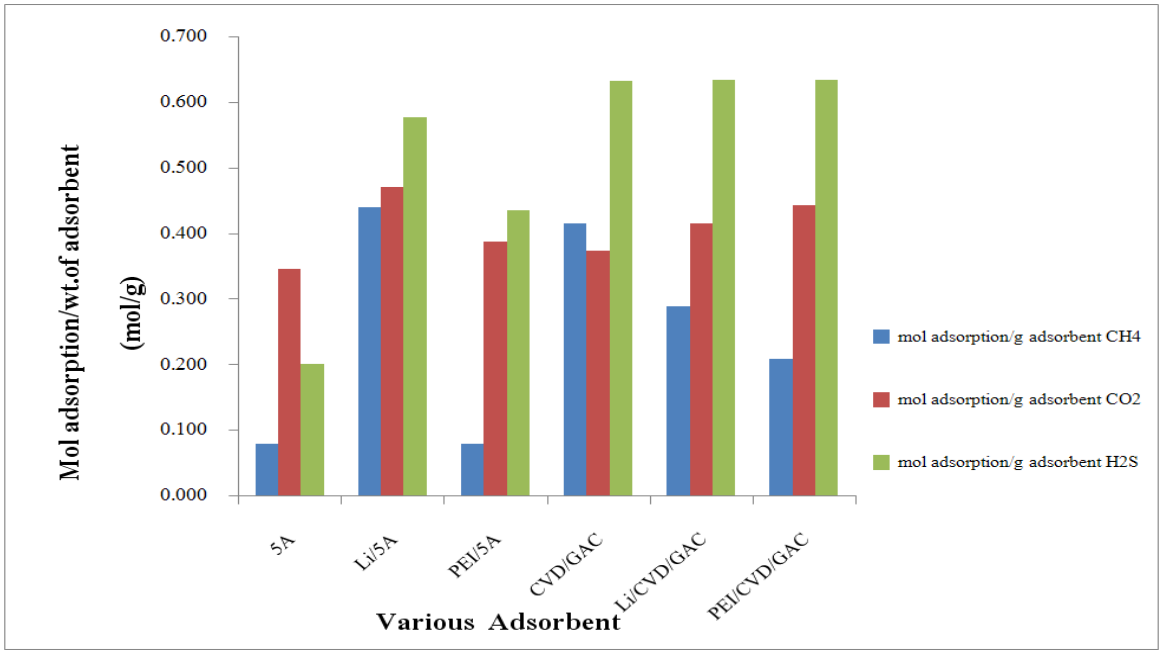

Figure 3. Adsorption performance of various adsorbent for CH_4, CO_2 and H_2S adsorption.

The CO_2 and H_2S outlet concentration by using various adsorbents show that the GAC is the good performance for CH_4, CO_2 and H_2S adsorption. The impregnation method can improve the CO_2 and H_2S adsorption efficiency. For Zeolite 5A, the Li impregnated on zeolite 5A can improve for H_2S adsorption efficiency. For CMS (PEI/CVD/GAC) can improve for CO_2 and H_2S adsorption efficiency. The result of breakthrough curve of the CO_2 adsorption efficiency in GAC, CMS_{GAC} (PEI/CVD/GAC), Zeolite 5A and Li 5A zeolite were 85, 110, 120 and 150 min, respectively, as shown Figure 4.

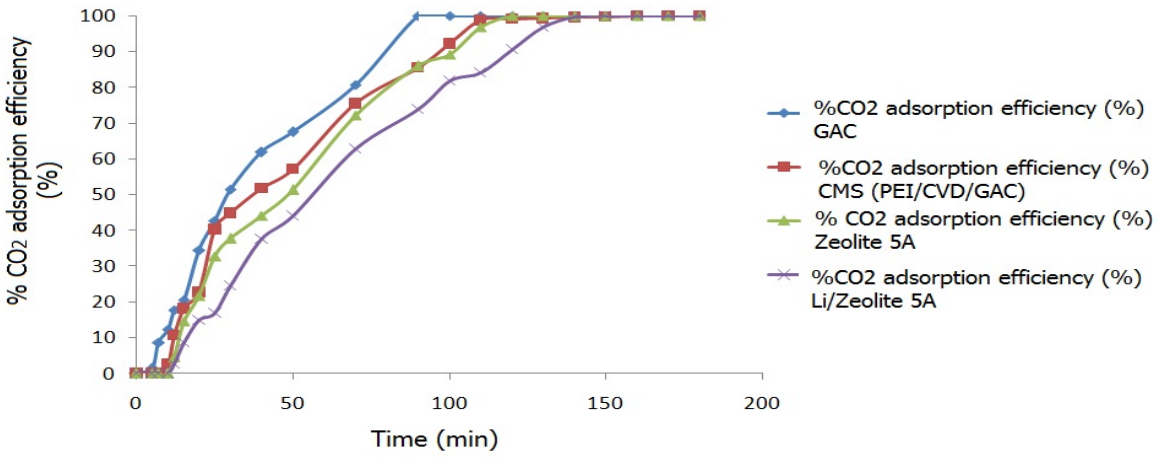

Figure 4. The breakthrough curve of the carbon dioxide adsorption efficiency by various adsorbents (GAC, Zeolite5A CMS_{GAC} ,and Li-zeolite 5A)

The analytical result of the purity of methane (CH_4) in synthesis mixed biogas for GAC, CMS_{GAC} (PEI/CVD/GAC) Zeolite 5A, and Li-Zeolite 5A were 81.53, 96.6, 93.6 and 97.26 %, respectively for the first cycle. The maximum cycle of purification for synthetic biogas is 7 cycles. The purity of methane gas (the outlet CH_4 concentration) of the various adsorbent results were shown in Figure 5.

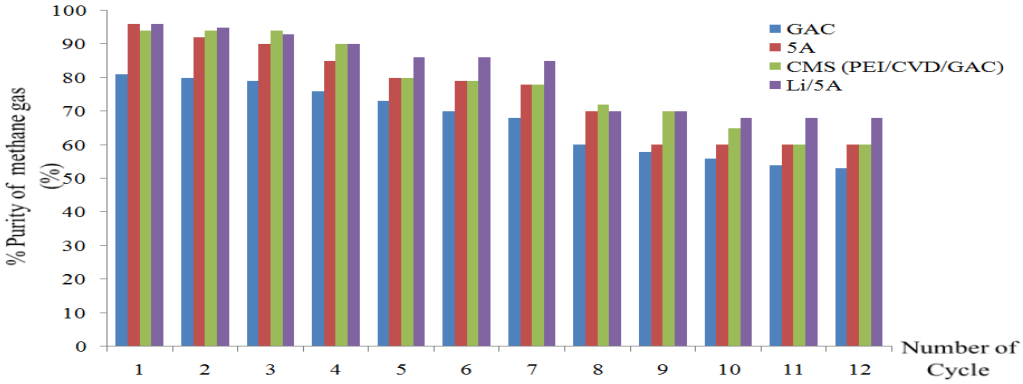

Figure 5. The purity of methane (CH_4) in synthesis mixed gas by various adsorbents (GAC, Zeolite 5A, CMS_{GAC}, and Li-Zeolite 5A)

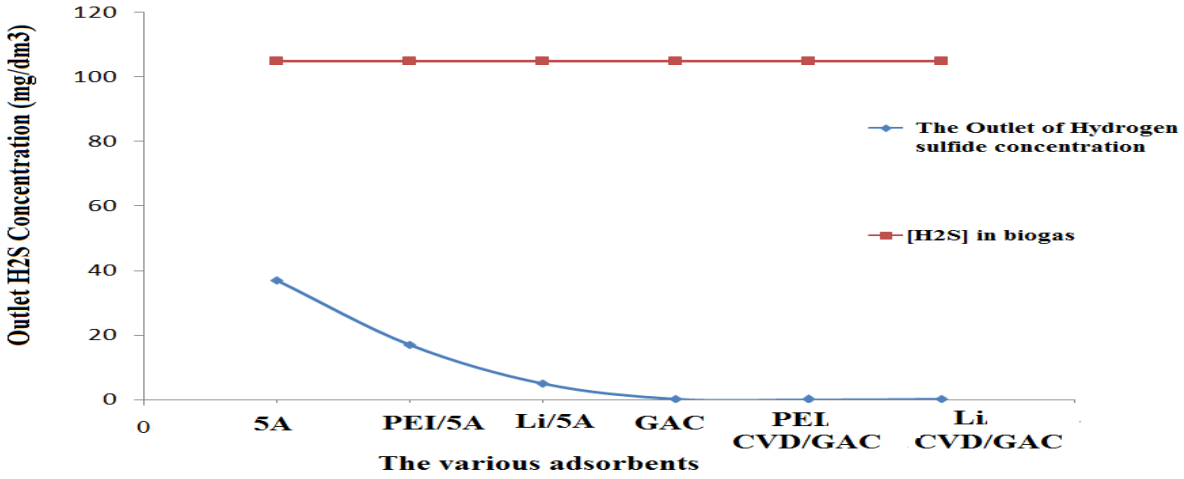

Figure 6. The outlet H_2S concentration in the synthetic biogas by using various adsorbent (GAC, CMS_{GAC} (PEI/CVD/GAC), CMS_{GAC} (Li/CVD/GAC), Zeolite 5A, Li-Zeolite 5A and PEI/Zeolite5A)

The result of the outlet H2S in biogas for GAC, CMS_{GAC} (PEI/CVD/GAC), CMS_{GAC} (Li/CVD/GAC), Zeolite 5A, Li-Zeolite 5A and PEI/Zeolite5A 0, 0, 0, 37, 5 and 20 mg/dm^3, respectively for the first cycle at the low concentration of H_2S. It can show in Figure 6. From the result show the unique pore structure of GAC and PEI impregnated on CVD/ GAC which is the amine on solid adsorbent can remove the low concentration of outlet H_2S.

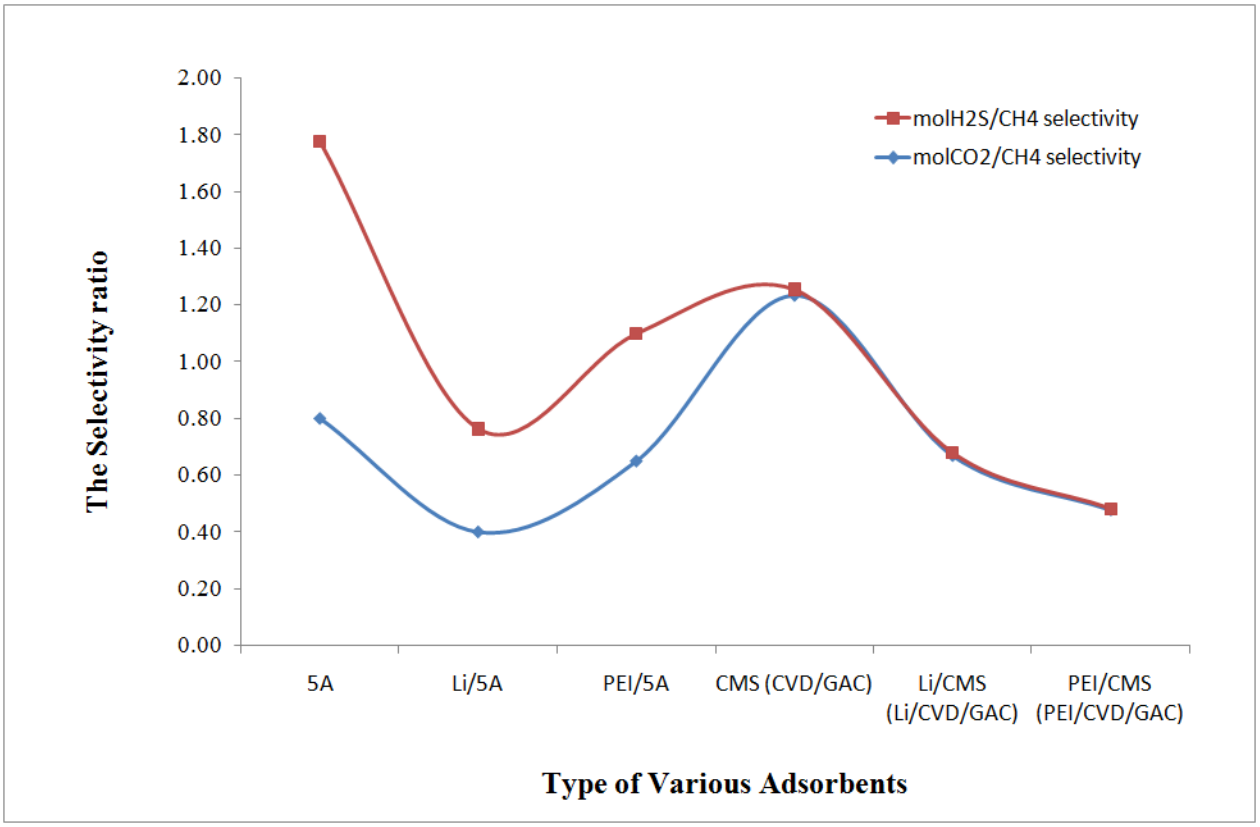

Figure 7. The Selectivity ratio by using the various adsorbents (Zeolite 5A, Li/5A, PEI/5A, GAC, Li/CMS_{GAC}, (Li/CVD/GAC) and PEI/CMS (PEI/CVD/GAC)

The Selectivity performance of the ratios between CO_2 and CH_4 is Li 5A zeolite and the selectivity performance of the ratios between H_2S and CH_4 is PEI/CVD/GAC as shown in Figure 7. The data indicate that the impregnation process on zeolite 5A can improve the oxidizing ability. The alkaline metal impregnation process has been improved the H_2S adsorption efficiency.

CONCLUSION

The Carbon molecular sieve by using PEI/impregnated on granular activated carbon by chemical vapor deposition process on granular activated carbon could improve the CO_2 and H_2S adsorption efficiency. Moreover, the lithium

impregnated on zeolite 5A is the good adsorbent for H_2S removal.

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