

Adsorption of CO₂ and Methane on Covalent Organic Polymer

Siew-Pei Lee¹, N. Mellon^{1,*}, Azmi M. Shariff¹ and Jean-Marc Leveque²

¹Chemical Engineering Department, Universiti Teknologi PETRONAS, 32610 Bandar Seri Iskandar, Malaysia

²LCME, Universite de Savoie Mont-Blanc, 73376 Le Bourget du Lac cedex, France

Abstract. Development of covalent organic polymer (COP) is a potential new class of adsorbent for CO₂ separation from natural gas mainly due to their good hydrothermal stability, chemical tuning flexibility and low cost. CO₂ and methane adsorption on COP-1 was studied under atmospheric condition (101.3 kPa, 298 K). COP-1 was synthesized via catalyst-free polycondensation of cyanuric chloride and piperazine. The properties of COP-1 were characterized using several analytical methods such as Fourier Transform Infra-Red (FTIR), N₂ adsorption and desorption measurement and Field Transmission Electron Microscopy in coupled of Energy Dispersive X-ray Spectroscopy (FESEM-EDS). Reversible CO₂ adsorption isotherm on COP-1 reflects low heat of adsorption which is beneficial to energy minimization in adsorbent regeneration process. Furthermore, moderate specific surface area COP-1 (88.5 m²/g) shows about nine times CO₂ uptake higher than methane. The highly selective adsorption performance provides a promising insight in application of COP adsorbent for CO₂ removal in natural gas field.

1 Introduction

Removal of CO₂ from gas reservoirs is highly important since the presence of CO₂ can cause operational problem such as solid formation and top-line corrosion in wet-gas pipelines (1). CO₂ is also an inert gas that reduces the heating value of natural gas and the amount of gas available for sales. Thus, CO₂-content must be minimized to within 2% - 3% by volume in order to meet the standard for compositional specification on pipeline gas (2).

Currently, the common method for CO₂ removal from natural gas is via chemical absorption process using alkanamine. However, this technology is subjected to operational drawbacks such as high rate of corrosion on equipment, degradation of solvent through oxidation, high energy consumption for regeneration and large absorber volume (3, 4). This drives the research for alternative gas treating technologies for CO₂ removal from natural gas reservoirs that is robust with higher removal efficiency and low operational problems. Among the possible emerging technologies, selective adsorption process is one of the most promising approaches because of the intrinsic eco-compatibility and flexibility such as zero regeneration of chemical solvents and applicability in relatively wide range of temperatures and pressures (5). In all adsorption technologies, the separation efficiency and adsorption capacity drive the selection of adsorbing material. Discovery of metal organic framework (MOF) (6, 7) and microporous organic polymer (MOP) such as covalent organic framework (COF) (8) and covalent organic polymer (COP) (9-11) are among the breakthroughs in alternative adsorbent development. These materials are very flexible in terms of structure tuning and properties through rational chemical design

and synthesis. For example, the recently generated COP-1 (10) has a great potential in CO₂ removal from natural gas stream with high hydrothermal stability, promising CO₂ adsorption capacity and good adsorbent recyclability. COP-1 was obtained by the polymerization of cyanuric chloride (CC) and piperazine as shown in Fig. 1. Free of metal catalyst in the synthesis offers some of the advantages in material development such as low cost production and environmental friendly.

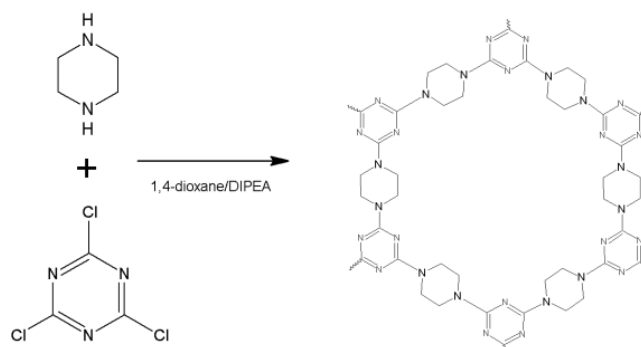


Fig. 1. Synthesis pathway of COP-1

Presently, available information for COP-1 is mainly concentrated on CO₂ removal in post-combustion process. However, scarce information on CO₂ removal from natural gas using COP adsorbent is reported in literature. Thus, the focus of this paper is to report the initial findings of the investigation on CO₂ removal from methane (CH₄), a representative of natural gas, using COP-1 at atmospheric condition

* Corresponding author: norhay@utp.edu.my

2 Methodology

Anhydrous cyanuric chloride (CC), piperazine and N,N-diisopropylethylamine (DIPEA) were purchased from Sigma Aldrich, USA. Dry 1,4-dioxane solvent with $\leq 0.005\%$ water content and ethanol were purchased from Merck Milipore.

CC (5.00 g, 27.1 mmol) was dissolved in dry 1,4 dioxane (50 mL). The solution was then added dropwise to a solution of piperazine (3.73 g, 43.3 mmol) and DIPEA (18.9 mL) in 1,4-dioxane (150 mL) with continuous stirring at 288 K under N₂ atmosphere. Resulting white mixture was stirred at 288 K for 1 h and then for a further with 2 h at 298 K and then 21 h at 363 K. The off-white precipitate formed was washed with 1,4-dioxane and soaked with ethanol three times over a period of 12 h. COP-1 was obtained after the off-white slurry was dried at room temperature under vacuum for 2 h.

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded Thermo Scientific Nicolet iS 10 FT-IR Spectrometer using ATR technique for CC, piperazine and COP-1. The morphology and Energy-dispersive X-ray (EDX) analysis was performed by FESEM on a Carl Zeiss AG SUPRA 55 VP. N₂ adsorption isotherm was obtained using Micromeritics ASAP 2020 Surface Area and Porosity Analyser at 77 K after the samples had been degassed at 428 K for 5 h. Low pressure CO₂ and CH₄ adsorption (up to 101.3 kPa) at 298 K were measured by Belsorp-mini II, Japan. Sample was degassed under vacuum at 423 K for 5 h prior to analysis.

3 Results and Discussion

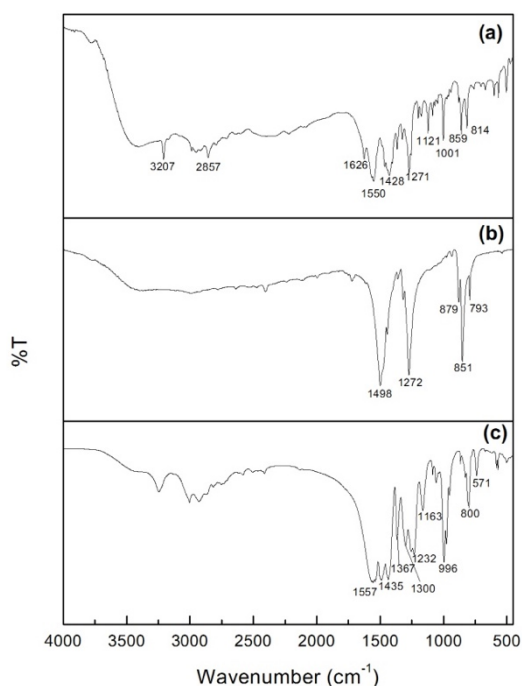


Fig. 2. FTIR spectra of (a) Piperazine (b) Cyanuric Chloride (c) COP-1

FTIR spectra, present the functional groups of CC, piperazine and COP-1. The characteristic stretching band for C-Cl functionality in the FTIR spectrum for CC is clearly visible at 850 cm⁻¹ [Fig 2(b)]. The disappearance of C-Cl stretching band in COP-1 structure [Fig 2(c)] suggested that all three chlorine atoms on CC were fully substituted. As a result, it is confirmed that the polycondensation reaction for COP-1 synthesis was fully completed in this study. Additionally, several strong peaks in the 1200-1600 cm⁻¹ region appeared in all three spectra, representing the stretching modes of CN heterocycles.

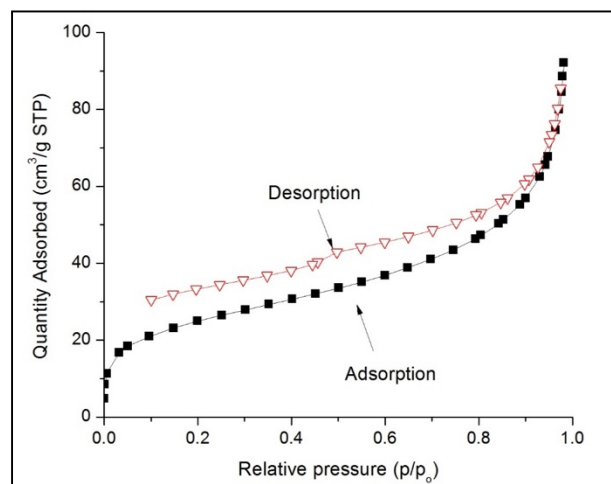


Fig. 3 N₂ adsorption-desorption isotherm

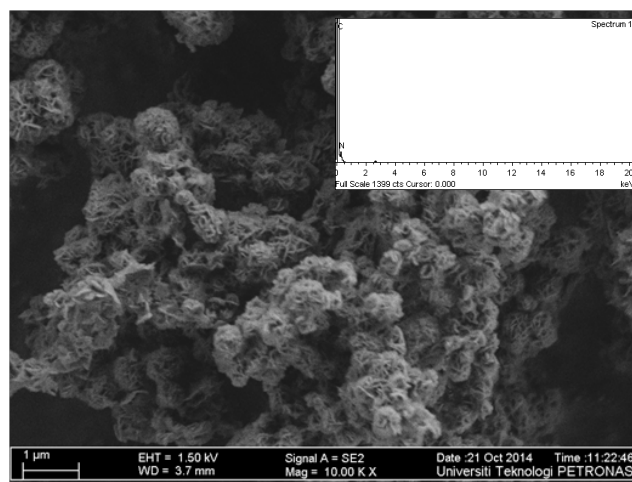


Fig. 4. FESEM micrograph of COP-1 (inserted: EDX analysis pattern)

Isotherm of COP-1 is plotted in Fig. 3 as the quantity adsorbed against the relative pressure. The isotherm is slightly convex at very low p/p, and no identification of a plateau as the relative p/p increasing (12). Hysteresis Type H3 loop was observed when desorption branch follows a different path and its appearance is due to the capillary condensation in mesopores. This isotherm is classified as Type IIb isotherm where the material forms aggregates of plate-like particles with non-rigid slit-shaped pores (13). Moderate specific surface area is observed in COP-1 i.e. 88.5 m²/g, calculated from the

linear part of the Brunauer-Emmett-Teller (BET) plot. Besides, about 9.7 nm of Barrett-Joyner-Halenda (BJH) desorption average pore diameter was found on COP-1.

FESEM micrograph Fig. 4 revealed the flaky and flower petals structure of COP-1. Bulk sphere structure is found to be due to the agglomeration of plate shape of the particles which is correlated to Type H3 hysteresis loop found in nitrogen isotherm. However, the bulk agglomerated spherical particle has limited the diffusion of gas molecules which highly attributes to low surface area of COP-1. The EDX analysis performed highlighted that no impurity was found on COP-1 other than C and N elements, as shown in inserted Fig. 4.

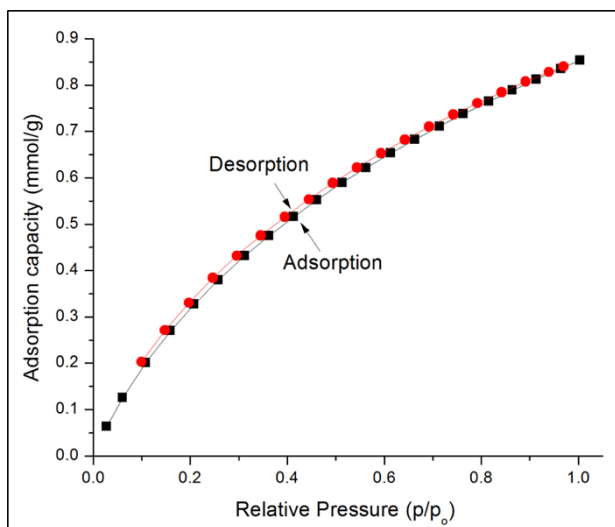


Fig. 5. CO₂ adsorption-desorption isotherm at 298 K

CO₂ isotherm on COP-1 for low pressure at 298 K is shown in Fig. 5. It is apparent that CO₂ molecules begin to fill in the mesopores at $p/p_0 \approx 0.03$. The increase of CO₂ adsorption on COP-1 as p/p_0 increases is because of the growth of clusters of molecules on the surface. Mesopores are filling with CO₂ adsorbates when the clusters merge together (14). Reversible isotherm without hysteresis in Fig. 5 reflects low heat of adsorption of the host for CO₂ adsorbates due to the affinity of physisorption for CO₂ is dominant on surface of COP-1 instead of chemisorption (15). This suggests that COP-1 with unique CO₂ adsorption isotherm competitive for energy minimization in adsorbent regeneration process compared to zeolites(16).

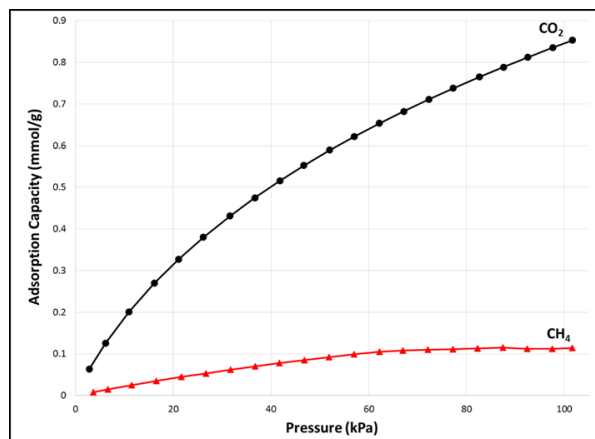


Fig. 6. CO₂ and CH₄ adsorption isotherms at 298 K

The CO₂ and CH₄ adsorption isotherms at 298 K of COP-1 are shown in Fig. 6. In this study, the CO₂ uptake i.e. about 0.9 mmol/g is significantly higher than CH₄ uptake (0.1 mmol/g) although both molecules are non-polar and display similar kinetic diameter (0.33 nm and 0.38 nm, respectively). It is interesting to note that the quadrupole moment of CO₂ moiety (4.30) is larger than CH₄ (0.02). Therefore, the interaction between the higher quadrupole moment of CO₂ molecules and dense electron cloud of nitrogen-rich network of COP-1 may facilitate CO₂ adsorption through the surface field gradient-molecular quadrupole interactions (5).

4 Conclusion

In conclusion, successfully synthesized COP-1 shows low adsorption energy for regeneration. At atmospheric condition, the dense electron cloud of polymeric network provides nine times of CO₂ uptake as compared to CH₄. It indicates that COP-1 possesses a great potential for CO₂ removal in natural gas field. Therefore, adsorption studies in wider range of temperature and pressure are necessary to evaluate its thermodynamic behaviour and CO₂ separation performance under natural gas drastic conditions.

Acknowledgement

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