

KAJIAN DFT DAN GCMC TERHADAP PENGARUH FUNGSIONALISASI ZIF-8 OLEH METILAMINA DAN ETILENDIAMINA PADA ADSORPSI CO₂ DAN SELEKTIVITAS CO₂/C₂H₂

Asma' Nadia Hanifah
22/498582/PA/21530

INTISARI

Telah dilakukan kajian mengenai pengaruh fungsionalisasi *Zeolitic Imidazolate Framework-8* (ZIF-8) menggunakan metilamina (MA) dan etilendiamina (ED) terhadap adsorpsi CO₂/C₂H₂ menggunakan metode *Density Functional Theory* (DFT) dan simulasi *Grand Canonical Monte Carlo* (GCMC). Fungsionalisasi ZIF-8 dimodelkan dengan menambahkan tiga gugus metilamina atau etilendiamina pada cincin imidazolat. Struktur ZIF-8, ZIF-8-MA, dan ZIF-8-ED kemudian dioptimasi menggunakan metode DFT pada tingkat GGA-PBESol dengan koreksi dispersi Grimme D3. Distribusi muatan atom dianalisis menggunakan metode DDEC6, sedangkan interaksi adsorbat–adsorben dikaji melalui perhitungan energi adsorpsi. Kapasitas dan perilaku adsorpsi CO₂ serta C₂H₂ dievaluasi menggunakan simulasi GCMC pada temperatur 298 K untuk memperoleh isoterm adsorpsi, parameter termodinamika adsorpsi, dan *Radial Distribution Function* (RDF). Data isoterm komponen tunggal kemudian diregresikan menggunakan model Langmuir–Freundlich dan digunakan untuk menghitung selektivitas adsorpsi CO₂/C₂H₂ dengan metode *Ideal Adsorbed Solution Theory* (IAST).

Hasil penelitian menunjukkan bahwa fungsionalisasi metilamina dan etilendiamina tidak mengubah topologi sodalit ZIF-8 dengan nilai RE parameter kisi < 0,50%. Penambahan gugus amina menghasilkan situs nitrogen yang lebih kaya elektron sehingga meningkatkan afinitas adsorpsi CO₂, yang tercermin dari energi adsorpsi yang lebih negatif pada ZIF-8-MA dan ZIF-8-ED dibandingkan ZIF-8 murni, masing-masing sebesar −40,41 kJ mol^{−1}, −34,64 kJ mol^{−1}, dan −18,2 kJ mol^{−1}. Peningkatan afinitas ini berkontribusi terhadap kenaikan kapasitas adsorpsi CO₂ pada 298 K, dengan urutan kapasitas adsorpsi ZIF-8-MA > ZIF-8-ED > ZIF-8, serta didukung oleh nilai koefisien Henry dan panas adsorpsi isosterik yang lebih tinggi. Analisis RDF mengindikasikan bahwa CO₂ tetap cenderung berada di sekitar ligan 2-metilimidazolat pada ketiga material. Perhitungan IAST menunjukkan bahwa seluruh material memiliki selektivitas CO₂/C₂H₂ di bawah satu, sehingga fungsionalisasi amina tidak meningkatkan preferensi adsorpsi terhadap CO₂. Dengan demikian, fungsionalisasi metilamina dan etilendiamina efektif meningkatkan afinitas dan kapasitas adsorpsi CO₂ pada ZIF-8, tetapi tidak meningkatkan selektivitas adsorpsi CO₂ terhadap C₂H₂.

Kata kunci: adsorpsi, DFT, GCMC, ZIF-8

DFT AND GCMC STUDY OF THE EFFECT OF ZIF-8 FUNCTIONALIZATION WITH METHYLAMINE AND ETHYLENEDIAMINE ON CO₂ ADSORPTION AND CO₂/C₂H₂ SELECTIVITY

Asma' Nadia Hanifah
22/498582/PA/21530

ABSTRACT

A study was conducted to investigate the effect of Zeolitic Imidazolate Framework-8 (ZIF-8) functionalization using methylamine (MA) and ethylenediamine (ED) on CO₂/C₂H₂ adsorption through Density Functional Theory (DFT) calculations and Grand Canonical Monte Carlo (GCMC) simulations. The functionalization of ZIF-8 was modeled by introducing three methylamine or ethylenediamine molecules attached to the imidazolate ring. The structures of ZIF-8, ZIF-8-MA, and ZIF-8-ED were subsequently optimized using the DFT method at the GGA-PBESol level with Grimme D3 dispersion correction. Atomic charge distributions were analyzed using the DDEC6 method, while adsorbate–adsorbent interactions were evaluated through adsorption energy calculations. The adsorption capacity and behavior of CO₂ and C₂H₂ were evaluated using GCMC simulations at 298 K to obtain adsorption isotherms, adsorption thermodynamic parameters, and Radial Distribution Function (RDF). The single-component adsorption isotherm data were fitted using the Langmuir–Freundlich model and subsequently applied to calculate CO₂/C₂H₂ adsorption selectivity using the Ideal Adsorbed Solution Theory (IAST).

The results showed that methylamine and ethylenediamine functionalization did not alter the sodalite topology of ZIF-8, as indicated by lattice parameter relative errors (RE) of less than 0.50%. The introduction of amine groups generated more electron-rich nitrogen sites, thereby enhancing the adsorption affinity toward CO₂, as reflected by the more negative adsorption energies of ZIF-8-MA and ZIF-8-ED compared with pristine ZIF-8, with values of -40.41 , -34.64 , and -18.20 kJ mol⁻¹, respectively. The enhanced adsorption affinity contributed to increased CO₂ adsorption capacities at 298 K, following the order ZIF-8-MA > ZIF-8-ED > ZIF-8, and was further supported by higher Henry's coefficients and isosteric heats of adsorption. Radial distribution function (RDF) analysis indicated that CO₂ remained preferentially located around the 2-methylimidazolate ligands in all three materials. Ideal Adsorbed Solution Theory (IAST) calculations showed that all materials exhibited CO₂/C₂H₂ selectivities below unity, indicating that amine functionalization did not improve the adsorption preference for CO₂ over C₂H₂. Overall, methylamine and ethylenediamine functionalization effectively enhanced the CO₂ adsorption affinity and capacity of ZIF-8 but did not improve its CO₂/C₂H₂ adsorption selectivity.

Keywords: adsorption, DFT, GCMC, ZIF-8