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Essid, M., Missaoui, N., Alnakhli, Z. et al (2025). One-step synthesis of mesoporous ZnO@ZIF-8 composites for CO<inf>2</inf>, CH<inf>4</inf>, N<inf>2</inf> adsorption and separation with potential application for industrial biogas. Journal of Alloys and Compounds, 1032. http://dx.doi.org/10.1016/j.jallcom.2025.181123

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Contents lists available at ScienceDirect

Journal of Alloys and Compounds



journal homepage: www.elsevier.com/locate/jalcom

One-step synthesis of mesoporous ZnO@ZIF-8 composites for CO₂, CH₄, N₂ adsorption and separation with potential application for industrial biogas

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ARTICLE INFO

Keywords: ZIF-8 ZnO@ZIF-8 composite Solid-state synthesis Adsorption Biogas purification

ABSTRACT

The separation of CO₂ and N₂ from CH₄ is essential for improving natural gas quality, while capturing and eliminating CO2 and CH4 from the air is crucial for reducing greenhouse gas emissions. This study investigates the performance of a mesoporous ZnO@ZIF-8 composite for these purposes by examining its adsorption equilibrium for CO₂, CH₄, and N₂. The composite was prepared through a mechanical grinding technique utilizing a mortar and pestle and characterized by various analytical methods, including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and nitrogen adsorption/desorption measurements. Adsorption isotherms for CO₂, CH₄, and N₂ were recorded at temperatures of 283, 298, 308, and 318 K and pressures up to 100 kPa, with the data being modeled using the Langmuir model. Additionally, separation selectivities for binary mixtures of CO₂/N₂, CO₂/CH₄, and CH₄/N₂, as well as biogas-like mixtures, were evaluated using the Ideal Adsorbed Solution Theory (IAST) model. At 298 K and 100 kPa, the selectivities for equimolar mixtures were found to be 9.13 for CO₂/N₂, 2.51 for CO₂/CH₄, and 3.63 for CH₄/N₂. Notably, the composite exhibited a CO₂ selectivity of 0.1086 at 283 K, which decreased to 0.0953 at 318 K, indicating the influence of temperature on CO₂ adsorption efficiency. Under these conditions, the adsorption capacities were measured at 3.0 mmol/g for CO2 and 1.3 mmol/g for CH4. These findings demonstrate the potential of the ZnO@ZIF-8 composite for efficient gas separation, particularly for enhancing biogas quality and contributing to greenhouse gas reduction through selective CO2 capture.

1. Introduction

Compared to other fossil fuels such as petroleum and coal, natural gas emits significantly less CO_2 per unit of energy, making it a comparatively cleaner energy resource [1]. However, impurities like CO_2 and N_2 present in natural gas can adversely impact its heating value and cause damage to pipelines and equipment due to corrosion [2]. To meet pipeline quality standards, the concentrations of CO_2 and N_2 in natural gas must be maintained below 2 % and 4 %, respectively [3]. As

a result, the efficient separation of CO_2 and N_2 from natural gas (primarily composed of CH_4) is crucial for the optimal use of low-quality natural gas sources, including biogas [4].

Greenhouse gases such as CO_2 and CH_4 are major contributors to global warming, with CO_2 alone being responsible for around 60 % of the total global warming impact. This significant contribution mainly results from industrial flue gases, which generally consist of approximately 70 % nitrogen and 15 % carbon dioxide [5]. Therefore, efficiently capturing and separating CO_2 from these emissions is essential

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https://doi.org/10.1016/j.jallcom.2025.181123

Received 29 March 2025; Received in revised form 19 May 2025; Accepted 21 May 2025 Available online 24 May 2025

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for minimizing its release into the atmosphere. On the other hand, methane (CH₄) possesses a much higher global warming potential (GWP) than CO₂, making it a particularly harmful greenhouse gas [6]. One of the major sources of methane emissions is landfill gas (LFG), where nitrogen levels can reach up to 20 % in certain cases [7]. As a result, the adsorption of CH₄ and its separation from N₂ are critical steps in reducing methane emissions and enhancing the quality of nitrogen-contaminated landfill gas.

A wide range of technologies has been explored for gas separation and purification, including cryogenic distillation [8], absorption [9], membrane separation [10], and adsorption [11-14]. Among these methods, adsorption has attracted substantial attention due to its superior energy efficiency, straightforward operation, and relatively low capital costs [3,15]. This technique is particularly appealing for separating binary gas mixtures like CO₂/CH₄, CH₄/N₂, and CO₂/N₂. Various adsorbent materials have been investigated for these applications, including clays [16], carbon-based materials [17–20], zeolites [21–23], silica's [24-27], metal-organic frameworks (MOFs) [28-32], and zeolitic imidazolate framework [11–14]. Silica materials, such as ASMS-3A, exhibit moderate CO₂ uptake capacities, reaching approximately 0.8 mmol/g at 283 K and 1 atm [24]. Zeolites like ETS-4 and ETS-10 show promise for natural gas upgrading, but their complex and lengthy synthesis processes present a significant challenge [23,33]. Metal-organic frameworks (MOFs) have also shown potential, with materials like MOF-177 displaying a CH4/N2 selectivity ratio of 4 and a methane adsorption capacity of 0.6 mmol/g at 298 K and 100 kPa [34]. Additionally, cobalt-based ZIF-67 demonstrates a CO₂/N₂ selectivity ratio of 3, achieving a CO2 adsorption capacity of 1.23 mmol/g under similar conditions [13]. Despite the promise shown by these materials, several issues remain unresolved. Many zeolites require substantial heat for regeneration, while others involve complicated synthesis procedures that hinder their practical application [35]. Therefore, there is an ongoing need to develop adsorbents that combine high adsorption capacity, effective selectivity, straightforward synthesis, and efficient regeneration to advance gas separation technologies [36].

Recently, mesoporous materials have gained considerable attention for their effectiveness in gas adsorption and separation [37-40]. Researchers have been actively investigating various mesoporous structures for enhancing adsorption performance. For example, Jiang et al. developed a hierarchical porous structure by combining graphene with ZIF-8 to form a Graphene/ZIF-8 hybrid aerogel, aiming to enhance CO2 adsorption efficiency by integrating microporous and mesoporous features [40]. Particularly, composites involving ZIFs or MOFs have emerged as promising candidates within the category of mesoporous materials. Their attractive properties include simple and scalable synthesis processes, high specific surface areas, large pore volumes, and tunable pore structures [37-43]. These features collectively make them highly suitable for a wide range of applications, including gas adsorption and catalytic processes [37-43]. As a result, developing advanced mesoporous composites continues to be a central focus in efforts to optimize materials for efficient gas separation and capture.

This study presents the development of a mesoporous ZnO@ZIF-8 composite synthesized using a novel, one-step method that has not been previously reported. The preparation process involves a straightforward mechanical grinding technique using a non-reactive agate mortar and pestle, providing a rapid and environmentally friendly synthesis approach that minimizes waste generation and reduces preparation time. Characterization of the composite was performed using various advanced techniques, including X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and nitrogen adsorption/desorption measurements to thoroughly examine its structural, chemical, and textural properties. Extensive gravimetric adsorption studies were conducted to evaluate the composite's capacity for adsorbing CO₂, CH₄, and N₂ at temperatures of 283 K, 298 K, 308 K, and 318 K under low-pressure conditions. The obtained adsorption data

were fitted to the Langmuir model, while the Ideal Adsorbed Solution Theory (IAST) was employed to estimate the separation performance for CO₂/N₂, CO₂/CH₄, and CH₄/N₂ binary mixtures. Additionally, the study calculated the isosteric heats of adsorption and performed dynamic breakthrough experiments to assess separation efficiency at different flow rates. One of the key innovations of this research is the detailed assessment of selectivity for CO₂, CH₄, and N₂ in biogas-like mixtures, including a thorough analysis of the CH₄/CO₂/N₂ system. The results indicate that the composite exhibits strong separation capabilities, particularly in enhancing methane purity by selectively removing CO₂ from CH₄. This work highlights the potential of eco-friendly materials for efficient gas separation and greenhouse gas reduction, demonstrating the benefits of the innovative synthesis method and comprehensive evaluation of its performance for practical biogas purification applications.

2. Experimental details

2.1. Material preparation and characterization

The chemicals utilized in the experiments, all obtained from Sigma-Aldrich without further purification, included zinc nitrate hexahydrate (Zn(NO3)2·6H2O; 98 % purity), methanol (99 % purity), 2-methylimidazole (HmIm; 99 % purity), and dimethylformamide (DMF; 99 % purity).

Characterization of microporous ZIF-8 and hierarchical porous ZnO@ZIF-8 hybrid composite structures was performed using several advanced analytical techniques. Phase identification was conducted through X-ray diffraction (XRD) using a Bruker D8 Discover Diffractometer. Surface area, pore volume, and pore size distribution were evaluated via N₂ adsorption-desorption isotherms with a Micrometrics ASAP-2420 surface area analyzer. Thermal stability analysis was performed using thermogravimetric analysis with a Perkin Elmer STA1000 instrument over a temperature range of 25–800°C at a heating rate of 5 °C/min. Sample morphology and particle size were examined by scanning electron microscopy (SEM) using a Philips XL30-FEG microscope. Additionally, FTIR spectra of powdered samples were recorded using a Perkin Elmer Spectrum Two FT-IR spectrometer with an attenuated total reflectance (ATR) accessory.

Gas adsorption experiments were carried out using an Autosorb-iQ-MP analyzer from Quantachrome Instruments, where the volume increase at equilibrium was measured relative to pressure. To ensure accuracy, sample weights were measured with a Sartorius BS-124S electrogravimetric balance, providing sensitivity to 0.1 mg. Approximately 100 mg of each sample was employed for adsorption tests involving CO₂, CH₄, and N₂ at temperatures of 283 K, 298 K, 308 K, and 318 K. Before performing the adsorption studies, all samples were degassed at 450 K for 12 hours to eliminate impurities and moisture. Temperature control during the adsorption tests was achieved using a TF-HX-5A refrigerated circulating bath from Shanghai Tian Feng Industrial Co., Ltd. The high-purity gases used for the experiments, including nitrogen (N₂, 99.999 %), carbon dioxide (CO₂, 99.995 %), and methane (CH₄, 99.994 %), were supplied by Air Liquide, France.

2.2. Separation of gas mixtures: CO₂/N₂ and CO₂/CH₄

Breakthrough experiments were conducted using CO_2/N_2 (50/50 v/ v) and CO_2/CH_4 (50/50 v/v) mixtures with a custom-designed setup depicted in Fig. 1. The dynamic separation process involved preparing 200 mg of activated ZnO@ZIF-8 hybrid composite material by heating it to 450 K for one hour under vacuum conditions. The prepared material was then packed into a stainless steel column with a length of 150 mm and an inner diameter of 10.0 mm. Following packing, the column was purged using helium gas at a flow rate of 20 Nml/min for 60 minutes at 298 K to remove any remaining impurities. After purging, pre-mixed CO_2/N_2 or CO_2/CH_4 gas mixtures were introduced into the column at a



Fig. 1. The apparatus used for testing the separation of CO₂/N₂ and CO₂/CH₄ gas mixtures.

flow rate of 0.5 Nml/min. The composition of the exiting gas was continuously monitored using a gas chromatograph equipped with a thermal conductivity detector (TCD) to precisely evaluate the separation performance. The efficiency of dynamic separation was assessed by analyzing the breakthrough curves generated for CO_2/N_2 and CO_2/CH_4 binary mixtures at 298 K. The tests were performed at various total flow rates of 10 Nml/min, 20 Nml/min, and 30 Nml/min to determine the influence of flow rate on separation efficiency.

2.3. Synthesis of ZIF-8 (Zn(MeIm)₂) crystals and ZnO@ZIF-8 composite

ZIF-8, represented chemically as Zn(MeIm)2, was synthesized using a solvothermal approach with N,N-dimethylformamide (DMF) serving as the solvent. The synthesis process involved dissolving 4.03 mmol (1.17 g) of zinc(II) nitrate hexahydrate and 3.65 mmol (0.88 g) of 2methylimidazole in 40 mL of DMF. The resulting solution was stirred for 20 minutes at ambient temperature in a 100 mL glass container to ensure thorough mixing. Following this, the prepared mixture was transferred to a 100 mL Teflon-lined autoclave, which was securely sealed and subjected to heating at 413 K for a duration of 24 hours to facilitate the crystallization process. Once the heating step was completed, the product was allowed to cool down and was then thoroughly washed three times with deionized water to eliminate any remaining solvent or unreacted materials. Finally, the cleaned material was dried at 403 K for 12 hours to obtain the purified ZIF-8 product. This synthesis method provides an effective route for producing highquality ZIF-8 with minimal impurities.

The porous ZnO@ZIF-8 composite was successfully synthesized through a simple and efficient solvent-free mechanochemical method. This approach involved grinding ZIF-8 precursor powders using a mortar and pestle for 10 minutes. The methodology relies on utilizing only porous precursor powders, which improves the efficiency of the solid-solid mechanochemical reaction and simplifies the overall process. After grinding, the resulting composite was carefully washed twice with deionized water to remove any remaining unreacted materials and by-products, ensuring the purity of the final product. The washing step plays a critical role in achieving a clean and high-quality composite. Following the washing procedure, the ZnO@ZIF-8 composite was dried overnight at 423 K in an oven. This drying step serves a dual purpose: eliminating residual moisture and activating the material. The final

product obtained was a white, porous ZnO@ZIF-8 composite, demonstrating the effectiveness of the solvent-free mechanochemical synthesis method.

3. Results and discussion

3.1. Structural and morphological characterization

3.1.1. X-ray diffraction (XRD) analysis

The experimental procedure highlights a highly efficient synthesis of ZIF-8, achieved within roughly 10 minutes under ambient conditions. This rapid and straightforward process offers significant advantages in terms of reducing production costs and improving scalability, making it an attractive approach for large-scale applications. To evaluate the phase composition and crystallinity of the materials produced, including ZnO, ZIF-8, and the ZnO@ZIF-8 hybrid composites, XRD analysis was performed. The XRD results, presented in Fig. 2., provide valuable insights into the structural characteristics of the synthesized materials, confirming their successful formation and crystallinity. ZIF-8 is produced through the coordination of 2-methylimidazole (mIm) ligands with zinc ions, resulting in a crystalline, microporous three-dimensional structure. This material is classified as a MOF, which is characterized by its high surface area and tunable porosity. The XRD patterns for ZIF-8 display distinct diffraction peaks at 2θ angles of 7.7° (011), 10.5° (002), 12.9° (112), and 18.2° (222), among others, as depicted in Fig. 2. The observed peaks correspond to the characteristic cubic unit cell structure of ZIF-8 and are in agreement with previously reported patterns in the literature [44-46]. This consistency with documented XRD data verifies the successful synthesis of ZIF-8. The material's structure features a sodalite-like cage framework with a substantial void volume, which makes it particularly suitable for various applications, including gas storage and separation, due to its highly porous nature [11,12].

Following the grinding of ZIF-8 crystals at room temperature using a mortar and pestle for 10 minutes, new broad diffraction peaks appeared at 20 angles of 31.67° (100), 34.33° (002), 36.27° (101), 47.39° (102), 56.52° (110), 62.72° (103), 66.32° (200), 67.92° (110), and 68.98° (201). These peaks are characteristic of the hexagonal wurtzite structure of ZnO, which belongs to the space group P63/mmc (JCPDS 36–1451) [47]. The presence of these peaks confirms the successful formation of ZnO with its characteristic wurtzite crystal structure. This phase is



Fig. 2. XRD patterns of ZIF-8, ZnO and ZnO@ZIF-8 composite materials.

well-known for its distinct optical and electronic properties, particularly its direct bandgap, which makes it highly suitable for a wide range of applications, including photonic devices and catalytic processes.

The noticeable broadening of the peaks indicates that the synthesized ZnO particles are of nanometer-scale dimensions. According to Xray diffraction principles, such peak broadening is commonly associated with smaller crystallite sizes, as predicted by the Scherrer equation. The XRD analysis also confirms the successful incorporation of ZnO within the ZIF-8 matrix. While the crystalline structure of ZIF-8 remains intact, additional peaks corresponding to ZnO are evident, demonstrating the formation of a hybrid composite. The effective integration of ZnO nanoparticles into the ZIF-8 framework is expected to enhance the material's overall functionality, potentially leading to improved catalytic performance, increased photochemical stability, and superior gas adsorption capabilities.

3.1.2. Fourier transforms infrared spectroscopy (FTIR)

To investigate potential ZnO formation resulting from the grinding of ZIF-8, Fourier Transform Infrared (FTIR) spectroscopy was performed in addition to the XRD analysis discussed in Section 3.1. The FTIR spectra, presented in Fig. 3, provide further insight into the structural characteristics of the materials. In the FTIR spectrum of pure ZIF-8, a distinct absorption peak appears around 420 cm⁻¹, which is attributed to the Zn-N stretching vibration. This peak confirms the coordination between zinc ions and nitrogen atoms within the 2-methylimidazolate (mIm) ligands, highlighting the typical metal-organic bonding structure present in ZIF frameworks. Additionally, the FTIR spectrum reveals several significant absorption bands associated with the imidazole ring. Vibrations within the ring are detected in the range of 1350–1450 cm⁻¹, while the C=N stretching vibration is observed around 1590 cm⁻¹. Moreover, C-N stretching vibrations are identified at approximately 995 cm⁻¹ and 1145 cm⁻¹. These spectral features align well with previous reports in the literature, confirming the integrity of the ZIF-8 framework [48–51].

For the ZnO@ZIF-8 composites, the FTIR spectrum continues to exhibit the characteristic peaks associated with ZIF-8, indicating that the imidazole linker remains intact within the composite material. The preservation of these peaks confirms that the structural integrity of the ZIF-8 framework is maintained during the synthesis process. Moreover,



Fig. 3. FTIR spectrum of ZnO, ZIF-8 and ZnO@ZIF-8 composite.

the FTIR spectrum reveals additional broad absorption bands within the range of 400 cm⁻¹ to 500 cm⁻¹, which are attributed to Zn–O stretching vibrations. These newly detected peaks suggest the formation and successful incorporation of ZnO nanoparticles within the ZIF-8 structure. The appearance of these Zn–O vibrations provides clear evidence of the interaction between the ZnO nanoparticles and the ZIF-8 framework, demonstrating the creation of a composite material with potentially enhanced properties. [47]. The combined FTIR data provide evidence for the composite nature of ZnO@ZIF-8, demonstrating that the ZIF-8 framework remains intact while ZnO nanoparticles are effectively incorporated. This incorporation suggests that the hybrid material exhibits enhanced functionalities, potentially offering synergistic properties advantageous for applications such as adsorption and catalysis.

3.1.3. Scanning electron microscopy (SEM)

The morphology of a material plays a crucial role in determining its properties and suitability for various applications. The SEM image of ZIF-8, shown in Fig. 4(a), reveals that the particles exhibit a uniform hexagonal shape with well-defined and smooth crystal surfaces [52]. The presence of clearly distinguishable edges and facets confirms the formation of a well-ordered crystalline structure during synthesis. Furthermore, the particle size distribution, illustrated in the histogram (Fig. 4(b)), indicates that the synthesized ZIF-8 particles range between 4 and 10 $\mu m,$ with an average size of approximately 7 $\mu m.$ This consistency in particle size and shape suggests that the solvothermal synthesis approach effectively produces ZIF-8 microcrystals with high crystallinity and uniform morphology. Pristine ZIF-8 crystals exhibit uniform rhombic dodecahedral morphology with an average particle size of approximately 7 µm. In contrast, the ZnO@ZIF-8 composite presents nanoscale, irregular, and partially spherical structures with an average diameter of 42 nm. This morphological evolution results from the mechanochemical processing and ZnO incorporation, which disrupt the long-range order of the ZIF-8 framework. The presence of ZnO nanoparticles promotes the formation of mesopores within the microporous ZIF-8 matrix, generating a hierarchical porous architecture that enhances external surface accessibility and facilitates faster diffusion kinetics, advantageous for gas adsorption and separation.



Fig. 4. The SEM images of (a) ZIF-8; (b, c) ZnO@ZIF-8 composite, and corresponding particle size distribution curve (d).

In contrast, the SEM images of the ZnO@ZIF-8 hybrid composite, shown in (Fig. 4(b) and 4 (c) reveal an irregular morphology. The ZnO@ZIF-8 nanoparticles exhibit dimensions in the nanometer range, with an average particle size of approximately 42 nm. Additionally, some particles with larger dimensions, around 70 nm, display aggregation and a spherical structure. These findings are further supported by the particle size distribution curve presented in Fig. 4(d), which reveals that the particle sizes fall within the range of 20-70 nm, with an average size of approximately 42 nm. This nanoscale particle size suggests successful integration of ZnO within the ZIF-8 framework, contributing to the formation of a well-defined composite material. Additionally, the elemental composition of the synthesized ZnO@ZIF-8 composite was confirmed through EDS analysis, as shown in (Fig. 5). The EDS results clearly indicate the presence of zinc, carbon, oxygen, and nitrogen, confirming the material's compositional purity and successful synthesis. The absence of extraneous elements further supports the high purity of the composite.

Following the grinding of microporous ZIF-8 at room temperature, SEM images distinctly show ZnO@ZIF-8 nanoparticles with irregular, spherical morphology and reduced agglomeration. This grinding step aims to decrease the particle size of ZIF-8, enhancing its surface reactivity and uniformity. Subsequently, the introduction of ZnO nanoparticles into the ground ZIF-8 creates a hybrid composite material. This synergistic integration results in a material with enhanced performance characteristics.



Fig. 5. EDS spectrum for ZnO@ZIF-8 composite.

3.1.4. Thermogravimetric analysis

The thermal stability of ZIF-8 was assessed using TGA analysis, which revealed a three-stage weight loss process, as illustrated in Fig. 6. The first stage of weight loss occurs between 25° C and 150° C, corresponding to the release of physically adsorbed gases, such as water (H₂O) and carbon dioxide (CO₂), from the material's surface [12]. This weight reduction primarily results from the desorption of these weakly bound molecules. The second weight loss stage is detected around 250° C and is attributed to the removal of residual N,N-Dimethylformamide (DMF) that remains trapped within the pores of the ZIF-8 framework.



Fig. 6. Thermogravimetric analysis of ZIF-8, and ZnO@ZIF-8 composites samples.

This step indicates that the synthesis process may leave minor amounts of solvent within the material's porous structure. The final stage, observed between 350°C and 450°C, signifies the thermal decomposition and conversion of ZIF-8 into zinc oxide (ZnO) [12]. This transformation is further confirmed by XRD analysis conducted on the sample after heating to 800°C, where the emergence of distinct ZnO peaks confirms the complete structural conversion of the material (Fig. 2) [47]. The TGA results, in conjunction with XRD analysis, provide clear evidence of the thermal degradation pathway of ZIF-8 and its eventual conversion to ZnO at elevated temperatures.

When subjected to a heat treatment up to 800°C, pure ZIF-8 retained approximately 34 % of its initial weight. In comparison, the ZnO@ZIF-8 composites exhibited a higher residual weight of about 62 %. The onset of decomposition for pure ZIF-8 was observed around 375°C, while the ZnO@ZIF-8 composites began decomposing at approximately 413°C. This delay in decomposition onset indicates a substantial enhancement in thermal stability for the composite material. The enhanced thermal stability of the ZnO@ZIF-8 composites is likely due to the incorporation of ZnO particles within the ZIF-8 matrix. These ZnO particles function as ceramic reinforcements, providing additional structural support that improves the overall integrity and stability of the composite material. The presence of ZnO helps prevent the premature decomposition of the ZIF-8 framework under elevated temperatures, thereby increasing its thermal resilience and making the composite more suitable for hightemperature applications [47].

The integration of ZnO nanoparticles within the ZIF-8 framework creates a heterostructure that markedly delays the breakdown and structural collapse of ZIF-8 samples. This synergistic interaction between ZnO and the ZIF-8 matrix enhances the overall thermal stability of the composite material. As a result, the ZnO@ZIF-8 composites can endure significantly higher temperatures without undergoing decomposition. The increased thermal stability is especially critical for applications involving high-temperature environments, as it ensures that the ZnO@ZIF-8 composites maintain their structural and functional integrity under such challenging conditions. The presence of ZnO acts as a reinforcing agent, providing additional support and stability to the ZIF-8 framework, thereby extending its durability and effectiveness in various high-temperature applications [47].

3.2. Textural property analysis by N_2 adsorption/desorption isotherms

The porosity of ZIF-8 and ZnO@ZIF-8 composites was assessed through nitrogen adsorption-desorption isotherms. The Brunauer-

Emmett-Teller (BET) surface area (SBET), pore volume, and pore size data are provided in Table 1. Fig. 7(a) displays the N₂ adsorption and desorption isotherms for ZnO@ZIF-8 composites at 77 K. The pristine ZIF-8 exhibits IUPAC Type I isotherms characterized by a sharp adsorption increase at P/P° ranging from $10^{\text{-5}}$ to $10^{\text{-1}}$, with no observable hysteresis during desorption [11,12]. This behavior is typical of microporous materials. The dominant pore size of 1.09 nm, illustrated in the inset of Fig. 7, is indicative of the microporous framework [53]. The S_{BET} surface area of ZIF-8 is approximately 1718 m²/g, which is consistent with reported literature values and represents one of the highest surface areas among ZIF derivatives [53-55]. Its micropore volume measures around 0.64 cm³/g, further confirming the Type I isotherm profile typical for microporous structures. The pore size distribution (PSD), determined by the (NLDFT) method, shows a unimodal distribution ranging from 0.84 nm to 1.32 nm, with a predominant peak at 1.09 nm. This result further verifies the microporous nature of ZIF-8 [12]. Additionally, the fully reversible and reproducible N₂ adsorption-desorption isotherms demonstrate that the material maintains stable and permanent porosity.

In ZnO@ZIF-8 composite materials, the adsorption isotherms change from the typical Type I pattern, which is associated with microporous adsorbents, to a Type IV pattern featuring hysteresis. This shift suggests the coexistence of microporous and mesoporous structures resulting from the incorporation of ZnO [56]. The original ZIF-8 framework, characterized by an intrinsic pore size of 1.09 nm, experiences a reduction to 0.94 nm, accompanied by a decrease in intensity in the PSD. The mechanical grinding process applied to the ZIF-8 framework leads to structural disruption, causing a partial collapse of the micropores. Since ZIF-8 is primarily a microporous material, the grinding process negatively affects its micropore structure, resulting in a reduced micropore volume. The presence of ZnO further contributes to altering the overall porosity, leading to the formation of a composite with both microporous and mesoporous characteristics.

Following the incorporation of ZnO, new mesopores with diameters ranging from 2.03 nm to 3.37 nm are detected, as calculated from the adsorption-desorption isotherms (Fig. 7(b), inset). The formation of these larger mesopores is attributed to the fragmentation and rearrangement of the material's structure. The nitrogen uptake plateau and the S_{BET} decrease upon the integration of ZnO, which is likely due to pore blockage caused by ZnO particles growing within the ZIF-8 framework [57,58]. This growth interferes with the original microporous network, reducing available micropore space. Despite the overall decrease in micropore volume from $0.64 \text{ cm}^3/\text{g}$ (in pure ZIF-8) to 0.52 cm³/g, the mesopore volume in the ZnO@ZIF-8 composite increases (Table 1). However, the total pore volume remains relatively unchanged at approximately 0.45 cm³/g. The mechanical grinding process contributes to these structural changes by damaging the ZIF-8 framework, leading to a partial collapse of micropores and a reduction in SBET surface area. Simultaneously, grinding also creates new mesopores or exposes previously inaccessible ones, resulting in an increased external mesopore surface area. This structural alteration transitions the material from being predominantly microporous to a more hierarchical porous structure, combining micropores and mesopores. These changes highlight the formation of a hybrid material with a more complex pore

Table 1
The porosity properties of ZIF-8 and ZnO@ZIF-8 samples.

Samples	S _{BET} (m²/g)	Pore volume (cm ³ /g)			Average Pore
		V _{Total}	V _{Micro}	V _{Meso}	Size (nm)
ZIF-8	1718	0.69	0.64	0.05	1.9
ZnO@ZIF-8	1478	0.97	0.52	0.45	0.94, 2.49

 S_{BET} : BET specific surface area; V_{Total} : Total volume at $P/P^\circ=$ 0.99; $V_{Meso:}$ Mesopore volume calculated by BJH-plot analysis; $V_{Micro:}$ Micropore volume calculated by V_{Total} - $V_{Meso.}$



Fig. 7. Nitrogen adsorption (solid) and desorption (empty) isotherms and the corresponding pore size distribution of ZnO@ZIF-8 composite materials. Insert in (b) is an enlargement image.

architecture, effectively integrating the properties of both ZIF-8 and ZnO.

3.3. Adsorption study of CO₂, CH₄ and N₂ for ZnO@ZIF-8 composites

The adsorption/desorption isotherms for CO₂, CH₄, and N₂ on mesoporous ZnO@ZIF-8 adsorbents were measured at four temperatures (283 K, 298 K, 308 K, and 318 K) and pressures up to 100 kPa, as illustrated in Fig. 8. These isotherms exhibit excellent reversibility without any noticeable hysteresis, indicating that the adsorbed gas molecules can be fully released during the desorption process. This feature suggests that the ZnO@ZIF-8 composites can be efficiently regenerated by applying a vacuum, making them advantageous compared to certain zeolite and MOF materials [59]. Furthermore, none of the gases reach their saturated adsorption capacity within the tested pressure range, indicating the potential for enhanced adsorption under higher pressures. The isotherms for CO2 and CH4 show slight curvature, whereas the isotherms for N2 are nearly linear, suggesting that the adsorbent has good regenerability [60]. The higher adsorption affinity for CO2 is likely due to its considerable quadrupolar moment, making it interact more strongly with the adsorbent's surface. CH4 is adsorbed more effectively than N₂, which can be explained by the higher polarizability of CH₄ compared to N₂. These findings indicate that the ZnO@ZIF-8 composites have a strong preference for CO2 adsorption, followed by CH₄, while showing minimal affinity for N₂ [61].

Adsorption capacity is a key parameter for assessing the gas separation performance of an adsorbent. For the ZnO@ZIF-8 composites, the CO₂ uptake capacities at 100 kPa are measured as 2.69 mmol/g at 283 K and 2.25 mmol/g at 298 K Fig. 8(a)). These results are superior to those of several commonly studied ordered mesoporous adsorbents, such as SBA-15 (~0.6 mmol/g) [61], MCM-41(~0.75 mmol/g) [62], and CMK-3 (~1.7 mmol/g) [63] at 298 K and 100 kPa. Moreover, the mesoporous ZnO@ZIF-8 composite shows better CO2 adsorption capacity at 298 K and 100 kPa (2.25 mmol/g) compared to several microporous adsorbents, including ZIF-7 (0.46 mmol/g at 293 K and 100 kPa) [64], ZIF-67 (0.95 mmol/g at 298 K and 100 kPa) [65], ZIF-79 (1.41 mmol/g at 273 K and 100 kPa) [66], ZIF-8 (2.36 mmol/g at 298 K and 100 kPa) [67], and HKUST-1 (2.5 mmol/g at 298 K and 100 kPa) [68]. In addition, this composite demonstrates a higher CO₂ adsorption capacity than various MOFs such as UiO-66 (1.60 mmol/g at 298 K and 110 kPa) [69] and IRMOF-11 (1.80 mmol/g at 298 K and 100 kPa) [70]. However, the CO2 uptake capacity of ZnO@ZIF-8 is lower than that of some high-performance materials like meso-HKUST-1 (3.4 mmol/g at 298 K and 100 kPa) [71], Zn-MOF-74 (3.9 mmol/g at 298 K and 110 kPa) [72], and Co-MOF-74 (5.3 mmol/g at 298 K and 100 kPa) [72]. This comparison highlights that the ZnO@ZIF-8 composite exhibits promising adsorption properties, although further optimization may enhance its capacity even further.

The CO₂ uptake capacity of ZnO@ZIF-8 exceeds that of numerous adsorbents commonly employed for CO₂/CH₄ and CO₂/N₂ separations. Specifically, ZnO@ZIF-8 demonstrates superior performance compared to:

- Open-ended nitrogen-doped carbon nanotubes produced via direct pyrolysis of MOF, which achieve approximately 1.3 mmol/g at 273 K [73].
- Clays, with CO₂ uptake ranging between 0.4 and 1.2 mmol/g at 298 K [74].
- Silica molecular sieves, which exhibit a capacity of about 0.8 mmol/ g at 283 K [42].
- Commercial activated carbon, showing a CO₂ adsorption capacity of 0.89 mmol/g at 298 K [75,76].
- Several MOF materials, with CO₂ uptake values ranging from 0.8 to 1.6 mmol/g at 298 K [14,77].

These comparisons highlight the superior CO_2 adsorption performance of ZnO@ZIF-8, making it a promising candidate for gas separation applications, particularly for CO_2/CH_4 and CO_2/N_2 mixtures.

The mesoporous ZnO@ZIF-8 composite exhibits excellent CH₄ adsorption capacities, achieving 1.13 mmol/g at 283 K and 0.95 mmol/ g at 298 K, both measured at 100 kPa (Fig. 8(b)). These adsorption capacities are notably higher than those of various adsorbents previously tested for CH₄/N₂ separation. For example, ZIF-68, ZIF-69, and zeolite 5 A demonstrate CH₄ uptakes of approximately 0.8 and 0.5 mmol/g at 298 K [34,78–80]. Moreover, the CH₄ uptake capacity of ZnO@ZIF-8 at 298 K and 100 kPa is nearly double that reported for other high-surface-area materials like ZIF-8, UMCM-1, and MOF-177, despite their large BET specific surface areas ranging from 1200 to 3000 m²/g [81]. This superior performance indicates that the incorporation of ZnO into the ZIF-8 framework significantly enhances its ability to adsorb CH₄.

3.4. Separation of binary mixtures

IAST has been widely applied to predict the adsorption behavior of gas mixtures in various adsorbents, including mesoporous materials [81, 82]. In this study, IAST was employed to evaluate the selectivities of CO_2/N_2 , CO_2/CH_4 , and CH_4/N_2 binary mixtures on the mesoporous



Fig. 8. (a) CO_2 , (b) CH_4 and (c) N_2 adsorption isotherms measured at different temperature (283 K, 298 K, 308 K, and 318 K) on the ZnO@ZIF-8 composite samples; Adsorption (solid) and desorption (open) isotherms; Solid line: Langmuir equation model.

ZnO@ZIF-8 composite. The analysis was conducted using experimental pure-component adsorption isotherms, which were accurately fitted to the Langmuir equation model, described by the following expression:

$$q = -q_m \cdot \frac{K_L \cdot P}{1 + K_L \cdot P}$$
(1)

In this model, q (mmol/g) represents the amount of gas adsorbed at a

given pressure P (kPa), while q_m (mmol/g) denotes the monolayer adsorption capacity, and K_L is the Langmuir isotherm constant. The parameters q_m and K_L derived from fitting the experimental data to the Langmuir equation are provided in Table 2. Additionally, Henry's constants (K) were calculated by multiplying qmq_mqm and K_L and are also presented in the table. The Langmuir model provides an excellent fit for all the adsorption isotherms, with correlation coefficients R^2 exceeding 0.9989, as shown in Fig. 8. These fitted parameters were subsequently used to perform IAST calculations, following well-established procedures from previous studies [80].

The adsorption selectivities of CO_2/N_2 , CO_2/CH_4 , and CH_4/N_2 binary mixtures are calculated using the following equation:

$$S_{i/j} = \frac{x_i/y_i}{x_j/y_j} \tag{2}$$

Where:

- *S_{i/j}* is the selectivity of component i over component j in a binary mixture,
- *x_i* and *x_j* are the mole fractions of components i and j in the adsorbed phase,
- **y**_{*i*} and **y**_{*j*} are the mole fractions of components i and j in the gas phase.

The selectivities for equimolar binary mixtures at different temperatures (283 K, 298 K, 308 K, and 318 K) are shown as a function of pressure in Fig. 9. For the CO_2/N_2 binary mixture, the selectivity of CO_2 over N_2 consistently increases with rising pressure, as depicted in Fig. 9 (a). At a pressure of 100 kPa, the selectivity values reach 9.52 at 283 K and 9.13 at 298 K. These selectivity values are either higher than or comparable to those of other commonly studied adsorbents under similar conditions. For instance, MIL-47(v) exhibits a selectivity of 9 at 298 K, while nitrogen-doped hierarchical carbons display selectivities in the range of 5.7–8.4 at 298 K [82,83]. These favorable selectivity results highlight the promising potential of the synthesized mesoporous ZnO@ZIF-8 composite materials for efficient gas separation applications, particularly in processes requiring selective CO_2 capture.

For CO_2/CH_4 separation, the selectivity of CO_2 over CH_4 increases with pressure, following a trend similar to that observed for CO_2/N_2 separation, as illustrated in Fig. 9(b). At a pressure of 100 kPa, the $CO_2/$ CH_4 selectivity values are approximately 2.64 at 283 K and 2.51 at 298 K. The selectivity exhibited by ZnO@ZIF-8 is higher than that reported for various mesoporous materials, including MCM-41 silica [62], CMK-3 [84], SBA-15 [84], and CMK-5 [85]. It also surpasses the performance of several MOFs [73,81] and covalent organic frameworks (COFs) [70], which generally demonstrate CO_2/CH_4 selectivities ranging from 2 to 2.4 at 298 K. Furthermore, the selectivity of ZnO@ZIF-8 is comparable to that of commercial zeolites, such as H⁺ mordenite, Linde

Table 2

Langmuir-parameters of adsorption isotherms of CO₂, CH₄ and N₂ onto ZnO@ZIF-8 hybrid composite material at different temperature (283 K, 298 K, 308 K, and 318 K).

Adsorbates	T (K)	q _m (mmol/g)	K_L (kPa ⁻¹)	k (mmol/g. kPa)
CO ₂	283	3.212	0.00422	0.01355464
	298	2.520	0.00327	0.0082404
	308	2.091	0.00241	0.00503931
	318	1.828	0.00156	0.00285168
CH ₄	283	1.624	0.00315	0.0051156
	298	1.379	0.00238	0.00328202
	308	1.071	0.00207	0.00221697
	318	0.992	0.00178	0.00176576
N ₂	283	1.343	0.00106	0.00142358
	298	1.049	0.00086	0.00090214
	308	0.952	0.00067	0.00063784
	318	0.876	0.00056	0.00049056



Fig. 9. IAST-predicted adsorption selectivities for equimolar binary mixtures of CO_2/N_2 (a) CO_2/CH_4 (b) and CH_4/N_2 (c) on the ZnO@ZIF-8 hybrid composite materials.

4 A, and chabazite, which have selectivity values between 2.8 and 3.7 at 273 K [78]. Although the selectivity of ZnO@ZIF-8 is somewhat lower than the selectivity of SBA-15 and MCM-41 (\sim 5.5), its CO₂ uptake capacity is significantly higher than that of mesoporous silica under similar conditions [62,84].

Fig. 9(c) shows that the selectivity of CH_4 over N_2 gradually increases with pressure. At 298 K and 100 kPa, the ZnO@ZIF-8 composite

achieves a selectivity of 3.63, which is approximately double the selectivity reported for CMK-5 [85]. This value also exceeds the selectivities of other adsorbents such as ZIF-69 (\sim 3) and IRMOF-1 (\sim 2), and is comparable to the performance of ZIF-68, IRMOF-11, and Cu-BTC, which exhibit CH₄/N₂ selectivities ranging from 3.5 to 3.8 [79,82]. These findings highlight the superior performance of ZnO@ZIF-8 in gas separation applications, demonstrating its higher selectivity and adsorption capacity compared to various other adsorbents under similar conditions.

The gas separation performance of the mesoporous ZnO@ZIF-8 composite adsorbent was assessed by examining selectivities at various binary compositions, all kept at a constant bulk pressure of 100 kPa, as shown in Fig. 10. For CO₂/CH₄ and CH₄/N₂ separations, the selectivities remain nearly constant over a broad composition range (0.05-0.95), demonstrating a favorable trait for practical adsorption applications [81]. Such stability across varying compositions highlights the robustness and reliability of the ZnO@ZIF-8 composite as an adsorbent. In the case of CO₂/N₂ separation, the selectivity gradually decreases as the mole fraction of yN2 in the gas phase increases. However, even when vN_2 reaches 0.95, the composite maintains a selectivity value of approximately 16 at 298 K and 100 kPa. This performance is significantly better than or comparable to other adsorbents reported in the literature. For instance, CMK-5 [85] shows a selectivity of 4.50, ZIF-8 [12] achieves a selectivity of 7.35, and Zn-MOF (ZnDABCO) [86] demonstrates a selectivity of 8.50 under similar conditions.

3.5. Isosteric heat of adsorption

When evaluating gas adsorption processes, the isosteric heat of adsorption (ΔH_{ads}) is a critical factor. It helps estimate temperature changes during adsorption and serves as an indicator of an adsorbent's regenerability. Additionally, ΔH_{ads} can provide insights into the surface's energetic heterogeneity. The isosteric heat of adsorption for a single component as a function of surface loading can be determined using the Clausius-Clapeyron equation [68]:

$$\Delta H_{ads} = -RT^2 \left(\frac{\delta \ln(P)}{\delta T} \right)$$
(3)

In this equation, ΔH_{ads} (kJ/mol) represents the isosteric heat of adsorption, T (K) is the temperature, P (kPa) is the pressure, and R (8.314 J/(mol.K) is the gas constant. Assuming that ΔH_{ads} is independent of temperature, the integrated form of the equation is:

$$\ln P = \left(\frac{\Delta H_{ads}}{RT}\right) + \text{Constant}$$
(4)

In this study, the isosteric heats of adsorption for CO₂, CH₄, and N₂ were determined by plotting lnP against 1/T based on equilibrium isotherm data. The obtained values ΔH_{ads} are displayed in Fig. 11, providing insight into the strength of interactions between the adsorbent (ZnO@ZIF-8) and the individual gas molecules.

Fig. 11 (a) illustrates that the isosteric heat of adsorption for each gas shows a slight increase with increasing surface coverage. This trend is likely due to enhanced lateral interactions between adsorbate molecules as the adsorption loading rises. Such behavior indicates that the mesoporous ZnO@ZIF-8 composite materials possess a relatively uniform surface for the adsorption of CO₂, CH₄, and N₂, which contrasts with activated carbon, known for its greater energetic heterogeneity [87]. Fig. 11 (b) displays the heats of adsorption at zero loading for the three gases. The measured Δ Hads\Delta H_{ads} Δ Hads values at zero loading for the mesoporous ZnO@ZIF-8 composite are 25.09 kJ/mol for CO₂, 21.18 kJ/mol for CH₄, and 20.10 kJ/mol for N₂. Since all these values are below 80 kJ/mol, it confirms that the adsorption processes are predominantly governed by physical adsorption mechanisms rather than chemical adsorption, ensuring easy regeneration of the adsorbent [88].



Fig. 10. IAST-predicted selectivities for mixture CO_2/CH_4 (a), CH_4/N_2 (b), and CO_2/N_2 (c) on the ZnO@ZIF-8 hybrid composite materials at the pressure of 100 kPa.

The ΔH_{ads} values obtained for the mesoporous ZnO@ZIF-8 composite are lower than those reported for activated carbon [89,90], which is likely due to the larger pore size present in the composite material. Additionally, these values are lower compared to materials such as ZIF-8 [12], ZIF-67 [13], CMK-5 [85], HKUST-1 [68], silicalite [91], and zeolite 5 A [92]. The relatively low isosteric heats of adsorption indicate that the ZnO@ZIF-8 composite can be easily regenerated, which is a

favorable property for practical applications. The combination of high thermal stability, substantial adsorption capacity, adequate selectivity, and simple regeneration highlights the potential of the ZnO@ZIF-8 composite as an effective adsorbent for selectively separating CO_2/N_2 and CO_2/CH_4 binary mixtures.

3.6. Breakthrough experiments study of CO₂/N₂ and CO₂/CH₄ mixtures

To evaluate the practical applicability of mesoporous ZnO@ZIF-8 composite materials for CO₂ capture from flue gas and natural gas, dynamic breakthrough experiments were performed using CO₂/N₂ (50:50 v/v), CO₂/CH₄ (50:50 v/v) and CO₂/CH₄ (10:90 v/v) gas mixtures. These tests aimed to simulate the performance of the composite in a packed column configuration. Fig. 12 presents the breakthrough results obtained at atmospheric pressure and a temperature of 298 K. The experiments were carried out at varying flow rates of 10 NmL/min, 20 NmL/min, and 30 NmL/min to assess the effect of flow rate on the separation efficiency.

As shown in Fig. 12, the ZnO@ZIF-8 composite displayed effective separation of CO_2/N_2 (50:50 v/v), CO_2/CH_4 (50:50 v/v) and CO_2/CH_4 (10:90 v/v) mixtures. For the CO_2/N_2 separation at a flow rate of 10 NmL/min, Fig. 12 (a) reveals that nitrogen (N₂) passed through the column almost immediately, reaching saturation within 2.23 minutes. This rapid breakthrough suggests that N₂ adsorption on the ZnO@ZIF-8 composite is minimal. In contrast, CO_2 was retained much longer within the column, with a breakthrough time of 35.38 minutes and full saturation achieved at 49.25 minutes. This extended retention period indicates a significantly higher adsorption capacity for CO_2 compared to N₂. The marked difference in breakthrough times between the two gases clearly demonstrates the superior selectivity of the ZnO@ZIF-8 composite towards CO_2 , highlighting its potential for efficient CO_2/N_2 separation.

For the CO₂/CH₄ separation at 10 Nml/min, shown in Fig. 12 (b), methane (CH₄) broke through the adsorption column first. This early breakthrough supports the observation that CH₄ had weaker interactions with the adsorbent, consistent with its lower quadrupole moment and polarizability compared to CO₂ (13.4×10^{-40} C.m² and 29.1 $\times 10^{-30}$ m³, respectively). In this experiment, the breakthrough time for CO₂ was 18.69 minutes, while CH₄ broke through at 7.01 minutes. The differences in breakthrough times reflect the stronger interactions between CO₂ molecules and the pore sites of the ZnO@ZIF-8 composite. The dynamic separation of a CO₂/CH₄ gas mixture with a 10/90 vol ratio was investigated using the ZnO@ZIF-8 composite. The results, presented in Fig. 12 (c), demonstrate that the ZnO@ZIF-8 composite exhibits effective and practical separation performance under these dilute CO₂ conditions.

The data also showed that as the feed gas flow rate increased, the breakthrough times for both CO_2/N_2 (50:50 v/v) and CO_2/CH_4 (50:50 v/v) mixtures decreased, indicating a reduction in separation capacity. Despite this, the ZnO@ZIF-8 composite consistently exhibited efficient separation of both gas mixtures at all tested flow rates, as seen in Fig. 12.

In summary, the ZnO@ZIF-8 composite exhibited outstanding separation performance for CO_2/N_2 and CO_2/CH_4 mixtures under dynamic conditions. This high selectivity and efficient adsorption capacity make it a promising candidate for CO_2 removal in flue gas treatment and natural gas upgrading applications.

3.7. ZnO@ZIF-8 composite in industrial application for the biogas selectivity

Biogas is a gas mixture generated through the anaerobic digestion of biomass, primarily composed of methane (CH₄) and carbon dioxide (CO₂), with smaller amounts of nitrogen (N₂) and other trace gases. A typical biogas composition consists of approximately 60 % CH₄, 35 % CO₂, and 5 % N₂ [93]. The separation and enrichment of biogas to



Fig. 11. (a) Variation and (b) comparison of isosteric heats of adsorption at zero loading of CO₂, CH₄, and N₂ on the ZnO@ZIF-8 hybrid composite materials.

increase its methane content are essential for its effective utilization as a renewable energy source. A critical factor in this process is the adsorption selectivity of the sorbent material for individual biogas components, which directly influences the separation efficiency. For biogas purification, the adsorption selectivity of CO_2 relative to CH_4 and N_2 is particularly significant. Materials exhibiting high selectivity for CO_2 are more effective at removing carbon dioxide from biogas, thereby enhancing the methane content. ZIF-8 is a well-studied material for its gas adsorption properties, owing to its porous structure and favorable selectivity toward various gases. The selectivity of CO_2 with respect to CH_4 and N_2 in ZnO@ZIF-8 can be calculated using the following equation [94]:

$$S_{\text{Serafin-Dziejarski-X1}} = \frac{\frac{n_{X1}}{P_{X1}}}{\frac{n_{X2} + n_{X3}}{P_{X2} + P_{X3}}}$$
(5)

Where:

- X₁ is a gas adsorbed,
- n_{X1} is the amount of X_1 gas adsorbed,
- n_{X2} and n_{X2} are the amounts of X_2 and X_3 gases adsorbed, respectively,
- *P*_{X1}, *P*_{X2}, and *P*_{X3} are the partial pressures of X₁, X₂, and X₃ gas in the mixture, respectively.

Table 3 shows the adsorption selectivity of ZnO@ZIF-8 at different temperatures: 283 K, 298 K, 308 K, 318 K, based on the experimental data.

The calculation of CO₂ adsorption selectivity relative to the CH₄ and N₂ mixture on the ZnO@ZIF-8 composite as a function of temperature has revealed significant trends relevant to industrial separation processes. The analysis shows a consistent decline in CO₂ adsorption selectivity as the temperature increases. At a temperature of 283 K, the selectivity is measured at 0.1086, while at 318 K, it decreases to 0.0953. This temperature-dependent behavior is typical of physical adsorption processes, where lower temperatures enhance adsorption efficiency. The reason behind this trend is that, at lower temperatures, the kinetic energy of gas molecules is reduced, allowing stronger van der Waals interactions between the gas molecules and the surface of the adsorbent [95].

The reduction in selectivity with increasing temperature can be attributed to the thermodynamic characteristics of the adsorption process. At lower temperatures, the Gibbs free energy of adsorption is more negative, indicating a more thermodynamically favorable process for CO_2 adsorption on the ZnO@ZIF-8 surface. Although higher temperatures result in increased entropy, the corresponding rise in kinetic

energy of gas molecules makes it more difficult for CO_2 molecules to overcome the energy barrier required to bind to the adsorbent surface. Consequently, at elevated temperatures, desorption becomes more likely than adsorption, reducing the overall effectiveness of the adsorption process and thereby decreasing selectivity [96,97].

Comparing the adsorption values of individual gases, it can be seen that CO_2 is preferentially adsorbed by ZnO@ZIF-8 over CH_4 and N_2 . This is due to the stronger electrostatic interactions and higher polarity of the CO_2 molecule, which makes it better bound to the pores of ZnO@ZIF-8. However, as temperature increases, this CO_2 adsorption advantage over other gases decreases, resulting in lower selectivity. In the context of industrial biogas purification, these results have important implications. The high CO_2 selectivity at lower temperatures suggests that gas separation processes should be optimized for lower temperature operation to maximize CO_2 removal efficiency. This may require the use of cooling systems, which incur additional operating costs, but the benefits of more efficient separation and higher methane purity may outweigh these costs.

3.8. Regenerability and recyclability of ZnO@ZIF-8 adsorbent material

To evaluate the regenerability of the ZnO@ZIF-8 hybrid composite material, multiple CO₂ adsorption experiments were conducted at a temperature of 298 K. The findings, illustrated in Fig. 13, clearly demonstrate that the composite's CO₂ adsorption capacity remains almost unchanged over five cycles. This stability indicates that the ZnO@ZIF-8 can maintain its adsorption capacity and is fully regenerable through repeated adsorption/desorption processes. Consequently, the material exhibits excellent recyclability for CO₂ capture, suggesting its potential applicability in industrial CO₂ capture systems.

The recyclability of the ZnO@ZIF-8 composite was assessed through five consecutive breakthrough experiments. After each adsorptiondesorption cycle, the composite was regenerated by purging it with helium gas at a flow rate of 10 mL/min at room temperature. The regeneration process continued until no detectable signals of CO_2 , N_2 , or CH₄ were observed, confirming the complete removal of the adsorbed gases.

Fig. 12 (d), 12 (e) and 12 (f) demonstrates that the ZnO@ZIF-8 composite's stable adsorption capacity over five cycles under controlled conditions, confirming its short recyclability. However, the long-term stability of the material remains an open question. Addressing this requires future research to test its durability over extended cycling and under realistic industrial conditions, including exposure to contaminants, thermal stresses, and varying operational parameters.

While the ZnO@ZIF-8 composite exhibits excellent recyclability and ease of regeneration, it is important to acknowledge that certain MOFs



Fig. 12. (a,b,c) Breakthrough separation curves and (d, e, f) regeneration performance of ZnO@ZIF-8 hybrid material for: (a) CO_2/N_2 (v/v 50:50), (b) CO_2/CH_4 (v/v 50:50), and (c) CO_2/CH_4 (v/v 10:90) mixtures at 100 kPa and 298 K.

Table 3CO2 selectivity of ZnO@ZIF-8 composite at different temperatures.

T (K)	283	298	308	318
CO ₂ Selectivity	0.1086	0.1083	0.1004	0.0953

and zeolites demonstrate superior CO_2 adsorption capacities under similar conditions. For instance, UiO-66-NH₂ exhibits a capacity of ~4.2 mmol/g at 1 bar and 298 K due to the presence of aminofunctionalized groups that enhance CO_2 interaction through chemisorption and physisorption [98]. Similarly, MOF-74 (Mg-MOF-74), known for its open metal sites, boasts a remarkable capacity of ~8.9 mmol/g at 1 bar and 298 K [99]. Among zeolites, Zeolite 13X demonstrates an impressive capacity of ~5.2 mmol/g at 1 bar and 298 K, attributed to its large pore size and cation exchange sites [100]. Zeolite 4 A, with a uniform microporous structure, achieves ~4.5 mmol/g, while Zeolite Y records a capacity of ~3.8 mmol/g under the same conditions, both benefiting from strong physisorption and dipole interactions [100,101]. These materials often outperform in terms of adsorption capacity due to higher surface areas, functional groups, or open metal sites. However, the ZnO@ZIF-8 composite offers unique advantages, such as ease of synthesis via a solvent-free, green method and excellent recyclability without the need for high-temperature regeneration. These attributes make it a promising



Fig. 13. Reusability of ZnO@ZIF-8 hybrid material for CO_2 adsorption at room temperature condition.

candidate for practical $\rm CO_2$ capture applications, especially in scenarios where cost-effectiveness and environmental sustainability are prioritized.

4. Conclusion

The extensive study of the mesoporous ZnO@ZIF-8 composite, synthesized via a facile solid-state methodology, underscores its considerable potential in gas separation technologies and greenhouse gas abatement. The composite was characterized by using advanced techniques, including XRD, FTIR, SEM, TGA, and nitrogen adsorption/ desorption measurements, revealing its favorable adsorption properties. Adsorption isotherms for CO₂, CH₄, and N₂, obtained at various temperatures and pressures, were accurately described by the Langmuir model. The composite exhibited remarkable selectivities for equimolar mixtures of CO_2/N_2 , CO_2/CH_4 , and CH_4/N_2 at 298 K and 100 kPa, with selectivity values of 18.26, 4.36, and 4.65, respectively. Additionally, the adsorption capacities were notably high, with CO2 uptake of 2.25 mmol/g and CH₄ uptake of 0.95 mmol/g. In the context of biogas comprising approximately 60 % CH₄, 35 % CO₂, and 5 % N₂ the ZnO@ZIF-8 composite demonstrates significant efficacy in enhancing methane purity through selective CO₂ removal. The CO₂ selectivity relative to CH₄ and N₂ exhibited a temperature-dependent variation, with values decreasing from 0.1086 at 283 K to 0.0953 at 318 K. This reduction in selectivity with increasing temperature is consistent with the principles of physical adsorption, where lower temperatures favor higher adsorption due to reduced molecular kinetic energy and enhanced van der Waals interactions between the gas molecules and the adsorbent surface. As temperature rises, increased molecular kinetic energy reduces the efficacy of adsorption, leading to a preference for desorption and a subsequent decrease in CO₂ selectivity. These findings underscore the importance of optimizing gas separation processes at lower temperatures to maximize CO₂ removal efficiency. Although this optimization may necessitate additional cooling infrastructure and incur higher operational costs, the resultant increase in methane purity and overall enhancement in biogas quality substantiate the investment. Although ZnO@ZIF-8 demonstrates excellent gas separation performance under dry and neutral laboratory conditions, its stability under industrial environments characterized by fluctuating humidity and the presence of acidic or alkaline contaminants requires further assessment. Literature indicates that ZIF-8 is relatively stable under moderate humidity and near-neutral pH but may degrade under strongly acidic conditions (pH < 4) due to hydrolysis of the Zn–N bonds. Similarly, ZnO

may exhibit changes in surface chemistry under extreme pH or high moisture levels. These aspects are critical for long-term deployment in biogas upgrading or post-combustion CO₂ capture, and ongoing work in our group is focused on evaluating the composite's durability under such stressors. Thus, the ZnO@ZIF-8 composite holds considerable promise for advancing biogas purification technologies and contributing to greenhouse gas mitigation strategies.

CRediT authorship contribution statement

Jarosław Serafin: Writing – review & editing, Visualization, Validation, Supervision, Investigation, Formal analysis, Data curation. Manel Essid: Validation, Methodology, Conceptualization. Zainab Hassan Alnakhli: Supervision, Methodology, Conceptualization. Nadhem Missaoui: Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Conceptualization. Hamza Khari: Writing – review & editing, Methodology, Conceptualization. Khadra B. Alomari: Writing – review & editing, Methodology, Conceptualization. Houcine Barhoumi: Writing – review & editing, Methodology, Conceptualization. Kanagat Kishibayev: Writing – review & editing, Data curation. Bartosz Dziejarski: Writing – review & editing, Data curation.

Data and materials

All data are included in the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors extend their appreciation to the Deanship of Research and Graduate Studies at King Khalid University for funding this work through Large Research Project under grant number RGP2/148/46. Jarosław Serafin is grateful for the financial support provided by the Generalitat de Catalunya through the AGAUR grant for Project No. 2023 CLIMA 00009 with the support of the Department of Research and Universities: the Department of Climate Action, Food and Rural Agenda; and the Climate Fund of the Generalitat de Catalunya.

Data availability

The data supporting the findings of this study are available from the corresponding author upon reasonable request. All experimental and computational data, including raw measurements, processed datasets, and analytical details, have been archived and can be provided for verification and further research purposes.

If applicable, publicly available datasets used in this study have been cited appropriately in the manuscript. Any additional data generated during the study that are not included in the main text or supplementary materials can be accessed upon request.

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