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A Highly Stable Microporous Covalent Imine Network Adsorbent for Natural Gas Upgrading and Flue Gas CO₂ Capture

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ABSTRACT

The feasible capture and separation of CO₂ and N₂ from CH₄ is an important task for natural gas upgrading and the control of greenhouse gas emissions. Here, we studied the microporous covalent imine networks (CIN) material prepared through Schiff base condensation and exhibited superior chemical robustness under both acidic and basic conditions and high thermal stability. The material possesses a relatively uniform nanoparticle size of approximately 70 to 100 nm. This network featured permanent porosity with a high surface area (722 m²g⁻¹) and micropores. A single-component gas adsorption study showed enhanced CO₂ and CH₄ uptakes of 3.32 mmol/g and 1.14 mmol/g, respectively, at 273 K and 1 bar, coupled with high separation selectivities for CO₂/CH₄, CH₄/N₂, and CO₂/N₂ of 23, 11.8 and 211, respectively. The enriched Lewis basicity in the porous skeletons favours the interaction of quadrupolar CO₂ and polarizable CH₄, resulting in enhanced CH₄ and CO₂ uptake and high CH₄/N₂, CO₂/CH₄ and CO₂/N₂ selectivities. Breakthrough experiments showed high CO₂/CH₄, CH₄/N₂ and CO₂/N₂ selectivities of 7.29, 40 and 125, respectively, at 298 K and 1 bar. High heats of adsorption for CH₄ and CO₂ (Q_{stCH₄}; 32.61 kJ mol⁻¹ and Q_{stCO₂}; 42.42 kJ mol⁻¹) provide the ultimate validation for the high selectivity. To the best of our knowledge, such a versatile adsorbent material that displays both enhanced uptake and selectivity for a

variety of binary gas mixtures, including CO_2/CH_4 , CO_2/N_2 and CH_4/N_2 , has not been extensively explored.

Keywords: CO_2 capture, Natural gas, Greenhouse gas, Adsorption, Porous organic polymer, Methane nitrogen separation

1. Introduction

Natural gas (NG) refers to a gaseous fossil fluid that comes mainly from landfill gas (LFG) and biogas plants. It comprises approximately 50 to 85% CH_4 with the remainder mostly CO_2 , N_2 , H_2O and H_2S . [1] It is considered a valuable alternative fuel and clean energy resource compared with conventional fossil fuels, such as coal, crude oil, and petroleum because it is low-cost, clear-burning and results in less CO_2 release per energy unit. [2, 3] The concentration of CO_2 and N_2 impurities in NG can be up to 40%, and their presence will reduce the heating value, and acidic CO_2 will further cause equipment and pipeline corrosion. [3] To meet pipeline quality requirements, the concentrations of CO_2 and N_2 in NG cannot exceed 2 and 4%, respectively. [2, 3] Additionally, both CO_2 and CH_4 are major greenhouse gases, and their rapid accumulation in the atmosphere has had adverse effects on the environment, including global climate change and ocean acidification. [4] Approximately 60% of the global warming and climate change is associated with CO_2 release, mostly from flue gas emission sources, [1, 2] but CH_4 has a 20 times higher global warming potential (GWP) than CO_2 . [2, 5] LFG is the major CH_4 release source to the atmosphere. [2, 6] Hence, the separations of CO_2/CH_4 , CO_2/N_2 and CH_4/N_2 are major processes in CO_2 capture and NG upgrading. The existing aqueous amine scrubbing process can effectively remove CO_2 , but the process is energy-intensive and corrosive. [7] The separation of CH_4/N_2 is even

more challenging, and it currently relies largely on cryogenic distillation, which is again an energy-intensive process. Adsorption/separation by porous solid adsorbents has been proposed as a feasible alternative because in principle it can provide a more energy-efficient process.[7, 8] However, to improve the efficiency of the adsorption process and minimize the loss of CH₄, the adsorbent must have not only a high adsorption capacity but also a high selectivity. Material stability upon exposure to heat, vapour and chemicals are also important in practical applications. All of these requirements have posed great challenges to the adsorbent systems that are currently the subjects of intensive investigations, including metal-organic frameworks (MOFs),[9-11] covalent organic frameworks (COFs),[12-15] molecular organic solids,[16] activated carbon[17] and amine-functionalized silica.[18]

Recently, a group of triazine-based porous materials has exhibited promising gas uptake and separation performance for the above mentioned gas separation systems, as well as superb robustness and thermal stability.[19-24] These materials are synthesized either through a high-temperature process in the presence of molten ZnCl₂ as both solvent and catalyst [19, 25] or through a milder solvothermal synthesis approach.[23, 26, 27] The stable triazine functional group not only contributes to the high material stability, but its high density of nitrogen also provides enriched Lewis bases that facilitate the adsorption of CO₂ and CH₄ but not N₂, and hence it enhances the selectivity of these separation systems.[8] Recently, Bhaumik and co-workers have developed microporous covalent imine network (CIN) material through a facile catalyst-free solvothermal synthesis procedure by using commercially available inexpensive melamine and 1,4-piperazinedicarboxaldehyde, and used as catalytic solid support.[28, 29] Still, the reported

CIN material is offering the open space to investigate the adsorbent proficiency for the ecologically essential gas uptake and separation applications. Because the CIN skeleton composition is quite interesting as it comprises plenty of Lewis base sites due to the simultaneous integration of triazine and piperazine component in a regular way, so it is expected to show superior uptake and separation performances for the CO_2/N_2 , CO_2/CH_4 and CH_4/N_2 systems. The resultant single-component gas adsorption study and breakthrough experiments indeed exhibited enhanced gas uptake and high CO_2/CH_4 , CH_4/N_2 and CO_2/N_2 selectivities. Commercially well-known amorphous materials, such as activated carbons, have long validated that crystalline order is not a prerequisite for gas capture, and it was established that amorphous organic microporous materials can be prepared as simple in a hyper cross-linked polymer (HCP) network.[8] Thus, CIN although being amorphous, can be considered a promising candidate for NG upgrading and CCS application owing to its facile and scale up synthesis, good robustness and thermal stability and superior separation characteristics. To the best of our knowledge, such versatile adsorbent material that exhibited coincident enhanced uptake and selectivities for varieties of gas mixtures, CO_2/CH_4 , CO_2/N_2 and CH_4/N_2 has not been well explored.

2. Experimental section

2.1 Materials

Structural monomers including melamine (99%), 1,4-piperazinedicarboxaldehyde (99%) and anhydrous dimethyl sulfoxide (DMSO) were purchased from Sigma-Aldrich. Solvents such as tetrahydrofuran (THF), 1,4-dioxane, chloroform (CHCl_3), ethanol, methanol (MeOH) and acetone were also purchased from Sigma-Aldrich. All of these chemicals were used without further purification.

2.2 Synthesis of the adsorbent

The porous CIN adsorbent material has been prepared by the modified procedure published elsewhere.[28, 29] Briefly, melamine (404 mg, 3.20 mmol) and 1,4-piperazinedicarboxaldehyde (684 mg, 4.8 mmol) were first charged to dissolve in 30 mL of degassed dimethyl sulfoxide (degassed by argon bubbling) in a flame-dried Schlenk flask fitted with a condenser through vigorous stirring. The clear solution was then allowed to reflux at 453 K for 72 h under an argon environment. After cooling to room temperature, the off-white precipitate was collected by filtration and thoroughly washed sequentially with dry DMSO, methanol, ethanol and excess acetone, THF and dichloromethane and finally dried in a vacuum oven at 120 °C. Then, the dried material was immersed in methanol, and the solvent was exchanged 2 to 3 times at 24 h intervals. The yield based on the total starting material is approximately 90%.

2.3 Characterization techniques

Transmission electron microscopy (TEM) images were taken on an FEI Tecnai twin microscope operated at 120 kV. The samples were first ground into a fine powder and dispersed in ethanol. The solvent evaporated, leaving the sample deposited on a 400-mesh copper TEM grid. Scanning electron microscopy (SEM) images were obtained using an FEI Nova Nano630 SEM and an FEI Helios NanoLab™ 600 DualBeam operated at 10 kV. The Brunauer-Emmett-Teller (BET) specific surface area was measured on an ASAP 2420 system (Micromeritics) using nitrogen at 77 K. Prior to all gas adsorption measurements, the samples were degassed at 453 K for 24 h under high vacuum. The pore size distribution was derived from the adsorption branch using nonlinear density functional theory (NLDFT). The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99. Single-component CO₂, CH₄ and N₂ adsorption isotherms were measured on an ASAP 2050 sorption analyser

(Micromeritics). XPS analysis was conducted on a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α X-ray source ($h\nu = 1486.6$ eV) operated at 150 W with a multi-channel plate and delay line detector under a vacuum of 10^{-9} mbar. All spectra were recorded using an aperture slot of $300\ \mu\text{m} \times 700\ \mu\text{m}$. The survey spectra were collected at a fixed pass energy of 160 eV. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out on a thermal analyser TG 209 (Netzsch), under N₂ flow (20 mL/min).

2.4. Breakthrough experiments

Mixture breakthrough experiments were carried out at 298 K with a setup shown in Scheme 1. Detailed information of the setup is available elsewhere.[19, 30, 31] In a typical experiment, 0.5 g of CIN sample was first packed into a solid disc using a hydraulic press under 15 bar. The disc was then broken down by a knife into small pieces of 30 to 40 mesh in size. The resulting pieces were packed into a quartz column (I.D. 5.8 mm, length 150 mm), and silica wool was used to seal the ends. The sample was activated in the column with a continuous helium flow (5 mL/min) at 453 K for 12 h. After that, the temperature of the column was decreased to 298 K and stabilized. Following this, the feed gas was switched from helium to a dry gas mixture of CO₂ and N₂ (15: 85, v/v) at 5 mL/min. The effluent gas was monitored by a mass spectrometer (Pfeiffer Vacuum, Germany). The absolute adsorption capacity of gas i (q_i) is calculated from the breakthrough curve using the following equation,

$$q_i = \frac{F_i \times t_0 - V_{dead} - \int_0^{t_0} F_e dt}{m} \quad (1)$$

where F_i is the influent flow rate of gas i (mL/min), t_0 is the total adsorption time (min), V_{dead} is the dead volume of the system (mL), F_e is the effluent flow rate of gas i (mL/min)

that is calculated from the mass spectrum signal, and m is the mass of the sample (g). The selectivity of the breakthrough experiment is defined as,

$$\alpha = (q_1/y_1)(q_2/y_2) \quad (2)$$

where y_i is the molar fraction of gas i in the gas mixture. Two CO₂:N₂ (v:v) feed compositions, 10:90 and 15:85, which are associated to the two boundary composition of flue gases.

Scheme 1: Schematic presentation of the laboratory breakthrough set up.

2.5. Calculation of isosteric heat of adsorption (Q_{st})

The CO₂ (and N₂; see supplementary information) adsorption isotherms measured at 273 K and 298 K were first fitted to the following Virial equation,

$$\ln p = \ln q + \frac{1}{T} \sum_{i=0}^m a_i q^i + \sum_{i=0}^n b_i q^i \quad (3)$$

where p is the pressure (bar), q is the adsorbed quantity (mmol/g), T is the temperature (K), R is the gas constant, a_i and b_i are Virial coefficients, and m and n represent the number of coefficients used to adequately fit the isotherms (herein, $m = 4$, $n = 3$). The isosteric heat of adsorption was calculated from the following equation,

$$Q_{st} = -R \sum_{i=0}^m a_i q^i \quad (4)$$

2.6. Selectivity calculation based on Henry's law

The CO₂/N₂ Henry selectivity was calculated from Henry's law under low pressure of up to 0.1 bar. The single component of both CO₂ and N₂ adsorption isotherms were fitted linearly up to 0.1 bar. Then, their slope ratio gives the corresponding selectivity of CO₂/N₂.

2.7. Selectivity calculation based on the ideal adsorption solution theory (IAST)

The single-component isotherms of CO₂ and N₂ were first fitted with dual site and single-site Langmuir isotherms, respectively, as follows,

$$q_i = q_{i,sat} \frac{b_i p_i}{1 + b_i p_i} \quad (5)$$

where q_i is the amount of adsorption of gas i (mmol/g), p_i is the bulk gas phase pressure (bar), $q_{i,sat}$ is the saturation adsorption capacity (mmol/g), and b_i is the Langmuir parameter (bar⁻¹). IAST assumes that Raoult's law is valid between the gas and the adsorbed phase,

$$p_i = p y_i = p_i^0 x_i \quad (6)$$

$$\sum_{i=1}^n x_i = \sum_{i=1}^n \frac{p_i}{p_i^0} = 1 \quad (7)$$

where p_i is the partial pressure of component i (bar), p is the total pressure (bar), y_i and x_i are the mole fractions of component i in gas and adsorbed phases, and p_i^0 is the equilibrium vapour pressure (bar). p_i^0 is calculated from the following equation,

$$\frac{\pi S}{RT} = \int_0^{p_i^0} \frac{q_i(p_i)}{p_i} dp_i = q_{i,sat} \ln(1 + b_i p_i^0) \quad (8)$$

Where π is the spreading pressure (assumed to be the same for all components), S is the specific surface area of the adsorbent (m^2/g), R is the gas constant, T is the temperature (K), and $q_i(p_i)$ is the amount of adsorption equilibrated with pressure p_i that is obtained from the single-component adsorption isotherm. The third term in equation (8) is the result after the single-site Langmuir isotherm (5) is applied. For binary mixtures, where $n = 2$, there are four unknown parameters S, π, p_1^0 and p_2^0 that can be determined by solving equations (7) and (8). The amount of adsorption in a mixture is found from the following two equations,

$$\frac{1}{q_T} = \sum_{i=1}^n \frac{x_i}{q_i(p_i^0)} = \sum_{i=1}^n \frac{1 + b_i p_i}{b_i p_i^0 q_{i,sat}} \quad (9)$$

$$q_i^{mix} = x_i q_T = \frac{p_i}{p_i^0} q_T \quad (10)$$

where q_T is the total amount of adsorption (mmol/g) and q_i^{mix} is the adsorbed amount of component i (mmol/g). The IAST selectivity S_{ads} is calculated from the following equation,

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \quad (11)$$

The IAST calculation is used to estimate the selectivity for the binary gas mixture containing 15% CO_2 and 85% N_2 , which is typically the flue gas composition.

3. Results and discussion

The CIN material was synthesized through a simple Schiff-base condensation of melamine and 1,4-piperazinedialdehyde at 453 K. A possible structure connection is shown in the Scheme 2.[28, 29]

Scheme 2: Schematic representation for the formation of porous covalent imine networks (CIN).

SEM and TEM images of the CIN particles are shown in Fig. 1, indicating that the particles have a relatively uniform morphology with a size of approximately 70 nm. Close inspection of the SEM images at high magnification reveals that these particles were composed of tiny spherical particles of approximately 5-10 nm in size (Fig. 1b). Furthermore, in the SEM analysis, no other morphologies were detected, implying the high yield of the nanoparticle-like morphology. The TEM images (Fig. 1c) also confirmed the nanoparticle architecture of the CIN, which agrees with the SEM image analysis (Fig. 1a-b). In the high-resolution TEM images (Fig. 1d), low electron density spots (pores) were observed throughout the specimen.[32] Thus, each nanoparticle comprised a microporous structure. The Schiff base reaction and the subsequent polycondensation between the triazine moiety of the melamine molecules and piperazine are very fast, so it is expected that the formation of porous structure is controlled kinetically instead of thermodynamically, which favours a highly porous but amorphous structure.[25, 33]

Fig. 1: FE-SEM images of CIN at low magnification (a) and high magnification (b); TEM images of CIN material at low magnification (c) and HRTEM image (d).

Fig. 2a shows the PXRD pattern of CIN. The broad diffraction peaks at approximately 2θ of 21.60° and 41.14° suggest that the CIN framework lacks of long range order and therefore is amorphous in nature.[34] To investigate the thermal stability of the CIN material, thermogravimetric analysis (TGA) has been carried out up to 1173 K at a ramping rate of 10 K min^{-1} under a continuous N_2 atmosphere, as shown in Fig. 2b. The studied CIN material showed high thermal stability, *i.e.*, it retained its structural stability up to 623 K although it was entirely composed of organic constituents. Up to 623 K, the material loses is about 15 wt.% and it should be due to the loss of adsorbed moisture and trapped solvent (DMSO) from the surface and pore interior. The material started to decompose at approximately 653 K and sharply decomposed until the

temperature reached 700 K. Increasing the temperature thereafter results in a relatively slow and gradual decomposition up to 1170 K.

Fig. 2: Powder X-ray diffraction (a) and TGA analysis (b) of the porous CIN material.

Fig. 3 shows the nitrogen physisorption isotherm, and the inset shows the pore size distribution of the CIN material. The isotherm is displayed as a typical type I curve, as defined by IUPAC. The sharp increase in the gas uptake at low relative pressures (P/P_0) up to 0.08 indicates the presence of a permanent microporosity.[8] The calculated BET and Langmuir surface areas are $722 \text{ m}^2/\text{g}$ and $785 \text{ m}^2/\text{g}$, respectively. No hysteresis was observed between the p/p_0 values of 0.40 and 0.85 in this material, confirming the absence of mesopores. The increase in the nitrogen uptake at relative pressures above 0.9 indicates the presence of macro-pores, originating from interparticle gaps or voids, as observed in the TEM and SEM image analysis.[8, 33] The isotherms are not completely closed at $p/p_0 = 0.20$. Such a feature has also been observed in non-crystalline microporous covalent organic frameworks that were reported recently.[12, 15]

Fig. 3: N_2 sorption isotherms of the CIN material measured at 77 K (Adsorption: filled circles and desorption: empty circles).

In addition to the thermal stability of the CIN material, we further investigated its stability towards humidity, air and/or acid or alkaline media. For example, the material was immersed in water for a week and in 1 M HCl or 1 M NaOH for 3 days. We investigated the materials by SEM and TEM image analyses, and it was observed that the materials retain their nanoparticle morphology, as shown in Figs. S1 and S2. Moreover, the CIN material is completely insoluble in water and all other common organic solvent.

The single-component adsorption isotherms for CO_2 , CH_4 and N_2 at different temperatures and 1 bar pressure and the corresponding selectivities are shown in Fig. 4. The CO_2 molecule is more polarizable and also has a higher quadrupole moment than the CH_4 molecule (Table 1), [35, 36] so it is expected that the CO_2 molecules will interact much more than the CH_4 molecules with the CIN framework which favours the capture of CO_2 over CH_4 . [8, 37] The calculated IAST selectivities based on the single-component adsorption study of CO_2/CH_4 (50:50; v/v) are 22, 15 and 9.5 at 273 K, 298 K and 323 K,

respectively (Fig. 4d and Table 2), and the selectivities in other compositions are as shown in Fig. S4b. The Henry's selectivities (< 0.1 bar) of CO_2/CH_4 are 18.7, 21.8 and 19.1 at 273 K, 298 K and 323 K, respectively (Table 2 and Fig. S5 and S6).[8, 12, 37] The obtained CO_2/CH_4 selectivity of the CIN materials is much higher than that of the reported similar adsorbent materials (Table 3), and this high-sorption selectivity performance upgrades the targeted clean-up of natural gas.

Table 1: Physical properties of CO_2 , N_2 and CH_4 gas molecules.

Gas Molecules	Kinetic Diameter ($\text{\AA}$)	Polarizability ($\times 10^{-25} \text{ cm}^3$)	Dipole moment ($\times 10^{18} \text{ esu.cm}$)	Quadrupole moment ($\times 10^{-40} \text{ cm}^2$)
CO_2	3.3	26.5	0	13.4
N_2	3.64	17.6	0	4.7
CH_4	3.80	26.0	0	-

The CO_2 and N_2 uptake isotherms are shown in Fig. 4a and 4c, respectively. In the experimental pressure range, the CO_2 uptake increases with the pressure and does not reach equilibrium or a saturated state.[2, 8] The CO_2/N_2 selectivity in the low-pressure range (< 0.1 bar) was estimated using Henry's law.[8, 12, 37] The linear plots of CO_2 and N_2 at 273 K and 298 K are shown in Fig. S5 and S6, and the calculated Henry selectivity (Table 2) at 273 K is 101, whereas at 298 K, it is 92, which is comparable to that of the reported materials (Table 3).[37] The decrease in the selectivity with temperature in the Henry regime could possibly be because that at higher temperature the interaction between host and guest molecules is reduced. The presence enriched Lewis base functionality in the porous skeleton of the CIN adsorbent intrinsically favours the interaction with CO_2 . In fact, the quadrupole moment of CO_2 is 2.85 times higher and its polarizability is 1.5 times more than those of N_2 (Table 1).[8, 35, 36] All of these

properties result in CO_2 interacting more favourably than N_2 with the CIN, which leads to a high CO_2 uptake capacity through the dipole and quadrupole interactions of CO_2 molecules as mentioned before.[8, 12] The IAST method was used to calculate the selectivity of CO_2 over N_2 for a 15/85 feed composition (model flue gas composition).[38] The obtained results are given in Fig. 4e, which shows that the selectivity of the CIN increases with the total feed pressure at a given temperature. This is because at low pressure most adsorption sites are unsaturated. So the IAST selectivity is close to single component Henry selectivity. With the rising pressure and loading, the competition for adsorption sites between CO_2 and N_2 intensifies; therefore the IAST adsorption selectivity rises due to the much higher affinity of CO_2 to the network. Such a preferable adsorption to CO_2 is confirmed in the mixture breakthrough studies that will be discussed later in Fig. 6. Similar phenomena was also reported in literature.[39] When temperature increases, the interaction of CO_2 to the network becomes weaker and therefore the selectivity will decrease at a given feed pressure, as shown in Fig. 4e as well as in Fig. S4c in ESI. At a total feed pressure of 1 bar, the estimated IAST selectivity ($\text{CO}_2:\text{N}_2$ 15:85) is 211 and 100 at 273 K and 298 K, respectively (Fig. 4e and Table 2).

Fig. 4: Single-component gas adsorption isotherms (close symbols for adsorption; open symbols for desorption) of the CIN material for (a) CO₂; (b) CH₄ and (c) N₂; Calculated IAST sorption selectivity of the CIN material (d) CO₂/CH₄ selectivity (CO₂: CH₄ 50:50; v/v) S1 at 273 K, S2 at 298 K and S3 at 323K; (e) CO₂/N₂ selectivity (CO₂: N₂ 15:85; v/v) S4 at 273 K and S5 at 298 K and (f) CH₄/N₂ selectivity (CH₄: N₂ 95:5; v/v) S6 at 273 K and S7 298 K.

Table 2: CO₂, CH₄ and N₂ uptake and CO₂/N₂, CO₂/CH₄ and CH₄/N₂ selectivities of the CIN material.

Entry	T (K)	Uptake (mmol/g) at 1 bar			Selectivity					
		CO ₂	CH ₄	N ₂	CO ₂ /N ₂		CO ₂ /CH ₄		CH ₄ /N ₂	
					Henry	IAST ^a	Henry	IAST ^b	Henry	IAST ^c
1	273	3.32	1.16	0.24	101	211	18.7	23	5.5	11.8
2	298	2.50	0.68	0.12	92	100	21.8	15	4.3	8.44
3	323	1.32	0.31	0.02	-	-	19.1	10	-	-

^a CO₂: N₂ (Flue gas composition) 85:15; ^b CO₂: CH₄ 50:50; ^c CH₄: N₂ 95:5.

The single-component CH₄ uptake isotherm and the CH₄/N₂ selectivity of the CIN adsorbent are shown in Fig. 4b and 4f, respectively. The material reversibly adsorbed and released CH₄ with a maximum uptake capacity of 1.16 mmol/g at 273 K and 1 bar, whereas its uptake capacity decreased to 0.68 mmol/g at 298 K and 0.31 mmol/g at 323 K at the same pressure. The observed high uptake capacity for CH₄ is possibly due to the presence of ample Lewis base functionalities which help the polarizable CH₄ molecules interact with the CIN material. The high Q_{st} for CH₄ (32.61 kJ mol⁻¹; Fig. 5a) also supports the high interaction of CH₄ molecules with the CIN framework, resulting in enhanced uptake and high CH₄/N₂ selectivity (Fig. 4b and Table 2). The CH₄ uptake (1.16 mmol/g) of the CIN material is much higher compared with the CH₄ uptake (0.5 mmol/g) of the reported microporous van der Waals crystals[40, 41] and similar reported solid

adsorbents (Table 3) and comparable to that of reported covalent organic cages.[12, 42] However, these reported materials can only be obtained from expensive starting monomers and harsh synthesis protocols, whereas the CIN material can be synthesized by following a facile synthetic pathway on a large scale from low-cost and commercially available starting materials. The marginal N_2 uptake and high CH_4 uptake of the CIN material results in a high CH_4/N_2 selectivity, making it of significant importance in natural gas upgrading applications. The calculated IAST selectivities of CH_4/N_2 (95:5; v/v) are 11.8 and 8.44 at 273 K and 298 K, respectively, and the Henry's selectivities are 5.5 and 4.3 at the same temperature, as shown in Table 2. The IAST selectivity plot at other compositions ($CH_4: N_2$ 90:10 and 50:50; v/v) and the Henry's plot are shown in Fig. S4a and Fig. S5 and S6, respectively.

The Q_{st} for the studied gases are calculated using Virial Eq. 3 and Eq. 4, and the obtained results for CO_2 , CH_4 and N_2 are as shown in Fig. 5a, 5b and 5c, respectively. The Q_{st} value calculated in the low uptake range (i.e., low-pressure range) represents the interaction strength between the gas and the adsorbent, i.e., CIN framework, whereas at higher loadings, it represents the interactions between the gas molecules. In the low loading range, the estimated Q_{st} values for CO_2 , CH_4 and N_2 are $42.42 \text{ kJ mol}^{-1}$, $32.61 \text{ kJ mol}^{-1}$ and $21.23 \text{ kJ mol}^{-1}$, respectively.

Fig. 5: Isosteric heats of adsorption of CIN for CO₂ (a), CH₄ (b) and N₂ (c) using Virial calculation.

Binary gas mixture breakthrough experiments were performed to demonstrate the effectiveness of the studied CIN material in real applications. The typical experiment was carried out at ambient pressure and temperature (1 bar; 298 K) under kinetic flow conditions with a model natural gas and flue gas mixture, as shown in Fig. 6. Natural gas sources such as landfill gas and biogas constitute approximately 50 to 85% CH₄ and CO₂. [1, 43] It is often more difficult to remove CO₂ from a dilute stream, so we performed the model breakthrough experiments at a CO₂:CH₄ composition of 15:85 v/v (Fig. 6a). The estimated adsorption capacities for CO₂ and CH₄ are 1.15 mmol/g and 1.0 mmol/g, respectively. The calculated CO₂/CH₄ selectivity is 7.29, which is very close to the IAST selectivity (Table 2). Fig. 6b shows the CH₄/N₂ breakthrough selectivity. The estimated uptake capacities for CH₄ and N₂ are 0.54 mmol/g and 0.085 mmol/g, respectively, at ambient temperature and pressure, and the CH₄/N₂ selectivity is 40, calculated using Eq. 2 as mentioned before. Thus, the observed breakthrough selectivity is much higher than the IAST selectivity of the CIN material. This result is very promising for natural gas upgrading applications.

Fig. 6: Column breakthrough experimental results for CIN material for different feed gas compositions (a) CO₂: CH₄ (15:85 v/v), (b) CH₄:N₂ (15:85 v/v) and (c) CO₂:N₂ (15:85 v/v), measured at 298 K and 1 bar after activation by continuous He flow at 473 K for 12 h.

In the measured CO₂/N₂ separation experiment, it was observed that the CIN material adsorbed CO₂ preferentially, and CO₂ breakthrough was observed after 10.3 min (Fig. 6c). The estimated adsorption capacities for CO₂ and N₂ are 1.03 mmol/g and 0.053 mmol/g, respectively, which correlate to a CO₂/N₂ selectivity of 125, calculated using Eq. 2. Thus, based on the observed breakthrough results under flue gas conditions, the CIN material showed a higher selectivity compared to the IAST selectivity, and this discrepancy is due to the intrinsic properties of the framework. The regeneration characteristics of the CIN material were also tested in breakthrough experiments by regenerating the material under relatively mild conditions with helium purging (5 mL/min, 353 K for 0.5 h). The regenerated material exhibits adsorption capacities similar to the CO₂/N₂ selectivity observed in the repeated breakthrough experiments. The obtained breakthrough curves can be split into three phases based on their adsorption characteristics,[44] as marked in Fig. 6. In phase I, the unsaturated CIN adsorbent simultaneously captured both CO₂ and CH₄ (Fig. 6a), CH₄ and N₂ (Fig. 6b), or CO₂ and N₂ (Fig. 6c) from the mixed gas feed stream. In phase II, the CIN continuously captured

CO₂ (in both Fig. 6a and Fig. 6c), but no more CH₄ (Fig. 6a) or N₂ (Fig. 6b and 6c) was captured, as the adsorbent had been saturated with CH₄ or N₂ in phase I. Moreover, in this phase, the CIN adsorbent may competitively and/or preferentially take up CO₂, while a portion of the adsorbed CH₄ (Fig. 6a) or N₂ (Fig. 6b and 6c) (that was adsorbed in the previous phase I) desorbs into the gas flow. This is a possible reason for the presence of extra CH₄ (Fig. 6a) or N₂ (Fig. 6b and 6c) molecules in the release stream in phase II. This observation suggests that the CIN material can selectively capture CO₂ over CH₄ and N₂ and CH₄ over N₂ from the mixed gas feed stream. In phase III, the flow rate and composition of the release stream are the same as those of the feed stream because the CIN was saturated with both from the previous phases.

For comparison purposes, Table 3 lists the CH₄ and CO₂ adsorption performances of various porous adsorbents recently reported in the literature.[2, 8, 12, 19, 45-52] The CH₄ uptake ranges from 0.63 to 1.3 mmol/g at 273 K and from 0.56 to 1.81 mmol/g at 298 K, and the Q_{st} ranges from 18.4 to 24.9 kJ mol⁻¹, whereas the CO₂ uptake from the listed materials ranges from 1.1 to 4.67 mmol/g at 273 K and from 0.27 to 4.41 mmol/g at 298 K, and the Q_{st} ranges from 16.5 to 35 kJ mol⁻¹. These solid adsorbents show CO₂/CH₄ selectivities ranging from 7 to 12 at 273 K and 3 to 8 at 298 K and CH₄/N₂ selectivities ranging from 7 to 16 at 273 K and 5 to 14 at 298 K and CO₂/N₂ selectivities from 20 to 113 at 273 K and 3 to 131 at 298 K. It was also observed that the successful grafting of the amine functionality to the adsorbent changed the CO₂ uptake (0.27 mmol/g to 2.0 mmol/g) and Q_{st} (26 kJ mol⁻¹ to 70 kJ mol⁻¹, Table 3), whereas the studied material showed a CH₄ uptake of 1.16 mmol/g and a CO₂ uptake of 3.32 mmol/g at 273 K and 1 bar, and the selectivities for CO₂/CH₄, CO₂/N₂, CH₄/N₂ are 23, 211 and 11.8, respectively

(Table 2). Thus, the comparison results demonstrate that the studied CIN material shows comparable or superior separation performance, which validates the improvement for the natural gas upgrading and CSS applications.

Table 3. Comparison of CO₂, CH₄ and N₂ storage aptitudes and CO₂/CH₄, CH₄/N₂ and CO₂/N₂, separation selectivities of different types of porous adsorbent reported in the literature with synthesized CIN material.

Material	Uptake (mmol/g) at 1 bar						IAST Selectivity at 1 bar						Q _{st} (kJ mol ⁻¹)			ref
	CO ₂		CH ₄		N ₂		CO ₂ /N ₂		CO ₂ /CH ₄		CH ₄ /N ₂		CO ₂	CH ₄	N ₂	
	273	298	273	298	273	298	273	298	273	298	273	298				
Temperature (K)	273	298	273	298	273	298	273	298	273	298	273	298	CO ₂	CH ₄	N ₂	
OMC	3.0	2.0	1.3	0.9	0.47	0.3	12.8	11.5	3.4	2.9	3.7	3.7	22	17.6	15.2	[2]
COP-3	3.30	-	-	-	0.125	-	151	-	-	-	-	-	24	-	-	[8]
PECONF-1	1.86	1.34	0.83	0.53	-	-	109	51	7	3	16	14	29	22.2	-	[12]
PECONF-3	3.49	2.47	1.0	0.58	-	-	77	41	10	8	7	5	26	24.9	-	[12]
PECONF-4	2.95	1.96	1.07	0.67	-	-	83	51	12	8	7	6	34	22.5	-	[12]
CTF-1	2.47	1.41	-	-	-	-	20	-	-	-	-	-	27.5	-	-	[19]
FCTF-1	4.67	3.21	-	-	-	-	31	-	-	-	-	-	35	-	-	[19]
C1M3-Al	4.11	-	-	-	-	-	24	-	-	-	-	-	20.9	-	-	[45]
COP-1 ^a	-	4.41	-	1.81	-	0.36	-	91	-	6.8	-	-	30.7	-	-	[46]
azo-COP-2	2.55	1.53	-	-	0.06	0.03	110	131	-	-	-	-	24.8	-	19.5	[47]
azo-COP-3	1.93	1.22	-	-	0.07	0.04	79	96	-	-	-	-	32.1	-	21	[47]
Azo-POF-1	2.98	1.88	-	-	0.19	0.16	52	37	-	-	-	-	27.5	-	-	[48]
PPF-3	2.09	-	0.63	-	-	-	20	-	9.2	-	-	-	21.8	19.4	-	[49]
BILP-2	3.39	2.36	0.88	0.56	0.12	0.09	113	71	10	7	-	-	28.6	18.4	-	[50]
[HC=C] ₅₀ -H ₂ P-COF	1.1	0.59	-	-	0.25	0.15	-	3	-	-	-	-	16.5	-	-	[51]
[EtNH ₂] ₁₅₀ -H ₂ P-COF	3.02	1.52	-	-	0.18	0.13	-	16	-	-	-	-	20.9	-	-	[51]
PAF-5	-	0.27	-	-	-	-	-	9.3	-	-	-	-	26	-	-	[52]
(10%) PEI-PAF-5	-	0.73	-	-	-	-	-	37	-	-	-	-	70	-	-	[52]
30% PEI-PAF5	-	2.0	-	-	-	-	-	403	-	-	-	-	66	-	-	[52]
CIN	3.32	2.50	-	-	-	-	211	100	23	15	12	9	42.2	32.7	21.0	This work

Q_{st} is an important parameter for adsorption. The studied adsorbent showed Q_{st} for CH_4 and CO_2 of $32.61 \text{ kJ mol}^{-1}$ and $42.42 \text{ kJ mol}^{-1}$, respectively, and to the best of our knowledge, these are the highest values for this type of material that are reported in the literature (Table 3). These reported materials include PECONF-1 to PECONF-3 ($22.2\text{--}24.9 \text{ kJ mol}^{-1}$),[12] PPF-3 (19.4 kJ mol^{-1}),[49] BILP-2 (18.4 kJ mol^{-1}),[50] azo-COP-1 to azo-COP-3 ($24.8\text{--}32.1 \text{ kJ mol}^{-1}$)[47] and NOP-19 to NOP-21 ($28\text{--}37 \text{ kJ mol}^{-1}$).[53] Very recently, by incorporating different functional groups (such as $EtNH_2$ or alkynes) a COF[51] adsorbent showed Q_{st} values ranging from 15.3 to 20.9 kJ mol^{-1} , and among other classes of materials, CMP-1-COOH (33 kJ mol^{-1})[54] and BILPs ($26.7\text{--}28.8 \text{ kJ mol}^{-1}$).[50]

Different MOFs, metal-exchanged MOFs and ZIFs were studied by Yaghi and his co-workers for the CO_2/CH_4 separation system using the breakthrough technique.[10, 31] Cu-BTC exhibited a CO_2/CH_4 breakthrough separation selectivity of 4.92 at 308 K and 1 bar,[55] whereas another Cu-BTC material showed a CO_2/CH_4 breakthrough separation of 8.1 at 303 K and 1 bar.[56] Zeolite 13X [57] showed a selectivity of 8, whereas ZIF-95 and ZIF-100 showed values of 4.3 and 5.9, respectively.[10] COF-6 showed a CO_2/CH_4 selectivity of 2.5.[13] For the CO_2/N_2 system conventional activated carbon and metal anchored activated carbon (KNC-A-K) have CO_2/N_2 selectivities of 4.5 and 44, respectively, as calculated from breakthrough experiments with a 10:90 v/v feed composition of CO_2/N_2 at 298 K and 1 bar.[30] Porous carbon monoliths with incorporated metal-organic frameworks (HCM-Cu₃(BTC)₂₋₃) showed selectivities ranging from 67 to 100.[44] Porous covalent triazine-based materials CTF-1 and fluorinated FCTF-1 exhibited breakthrough selectivities of 18 and 77, respectively,[19]

and MOFs such as SIFSIX-2-Cu-I exhibited an IAST selectivity of 140 and a breakthrough selectivity of 72.[58] Metal-doped materials such as Ni/DOBDC (Ni-MOF-74 or CPO-27-Ni) showed flue gas breakthrough selectivities ranging from 22 to 38.[59] In view of the above comparisons and progress, the CIN material exhibited comparable or higher performance than the best porous materials reported in the literature.

4. Conclusions

In conclusion, we worked on the Lewis-base-enriched and electron-rich novel microporous CIN material, synthesized by using low-cost and commercially available starting materials. This framework offers permanent porosity with a high surface area, exhibits superior robustness, and is stable to chemical and thermal treatments. The availability of Lewis base sites due to simultaneous integration of triazine and piperazine component enhances CO_2 and CH_4 uptake and their selective separations (i.e., CO_2/CH_4 , CH_4/N_2 and CO_2/N_2), as revealed by single-component gas adsorption studies and column breakthrough experiments, which can promote the clean-up of natural gas and flue gas CO_2 capture. The observed enhanced CO_2 uptake and CO_2/N_2 selectivity is due to quadrupole-dipole interactions between the CO_2 molecules and the Lewis base sites (lone pair of electrons on the electronegative nitrogen functionality). The high thermal and oxidative stability, low cost, and enhanced CH_4 uptake and high heats of adsorption as well as high selectivity CO_2/CH_4 and CH_4/N_2 broaden the window of upgrading natural gas (generally diluted with N_2). In addition, its high CO_2 uptake and high heats of adsorption as well as high selectivity for CO_2 over N_2 make the material a potential candidate for CSS application. Thus, the CIN material with its unique nanostructure and enhanced properties (stability, enhanced CH_4 , CO_2 capture and selectivity) can be a

promising candidate for use as an adsorbent for the clean-up of NG and environmental remediation.

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List of symbols

(P/P_0) = Relative pressure.

Q_{st} = Isothermic heat of adsorption (kJ mol^{-1}).

F_i = Influent flow rate of gas (mL/min).

F_e = Effluent flow rate of gas (mL/min).

q = Absolute adsorption capacity of gas (mmol/g).

α = Breakthrough selectivity of gases.

y = Molar fraction of gas in the gas mixture.

R = Universal gas constant (8.315 J/mol K).

q_{sat} = Saturation adsorption capacity (mmol/g).

q_T = Total amount of adsorption (mmol/g).

M = Molarity (mole/liter).

T = Temperature (K)

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GRAPHICAL ABSTRACT

A Highly Stable Microporous Covalent Imine Networks (CIN) Adsorbent for Natural Gas Upgrading and Flue Gas Capture

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The microporous CIN material offering superior chemical robustness under both acidic and basic conditions and high thermal stability. Framework enriched with Lewis basicity and high Q_{st} facilitated to enhance natural gas upgrading and flue gas CO₂ capture, make the material as a promising adsorbent.

HIGHLIGHTS

- ❖ The microporous covalent triazine-piperazine linked nanostructure with permanent porosity.
- ❖ Material comprises enrich Lewis base sites and showed outstanding chemical robustness and high thermal stability.
- ❖ The material acts as an adsorbents and showed enhanced CO₂ and CH₄ uptake and high CO₂/N₂ and CH₄/N₂ sorption selectivity.
- ❖ High heats of adsorption for CH₄ and CO₂ (Q_{stCH_4} ; 32.61 kJ mol⁻¹ and Q_{stCO_2} ; 42.42 kJ mol⁻¹) provide the ultimate validation for the high selectivity.
- ❖ The single-component gas adsorption study and binary gas mixture breakthrough experiment raised the material as a promising adsorbent.