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Monte Carlo simulation of adsorption isotherms on mesoporous silica materials

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Abstract

An observation that frames this research is that the accuracy of Monte Carlo (MC) simulation of gas adsorption in mesoporous materials depends critically on force field selection and pore geometry representation, yet many published simulations in this area use generic force field parameters without explicit validation against experimental data for the specific material under investigation. This research reports grand canonical Monte Carlo (GCMC) simulations of CO₂, N₂, and CH₄ adsorption isotherms on a model MCM-41 mesoporous silica at 298 K, validated against experimental N₂ physisorption and CO₂ adsorption data collected on a synthesised MCM-41 sample. Lennard-Jones parameters for silica framework atoms were taken from the TraPPE force field with partial charges assigned by periodic DFT. Simulated isotherms reproduced experimental CO₂ uptake within 6.8% and N₂ within 4.3% across the full pressure range. The CO₂/N₂ selectivity predicted by GCMC was 6.4:1 at 0.1 bar, suggesting that functionalised MCM-41 is a worthwhile candidate for post-combustion CO₂ capture. Isothermic heats of adsorption calculated by the Widom test particle method were 28.3, 14.7, and 21.6 kJ/mol for CO₂, N₂, and CH₄ respectively, consistent with physisorption on the hydroxylated silica surface.

Keywords: Monte Carlo simulation, adsorption isotherm, mesoporous silica, MCM-41, grand canonical, CO₂ capture, TraPPE force field, isosteric heat

Introduction

Mesoporous silica materials—most notably MCM-41 with its ordered hexagonal channels of 2-10 nm diameter—have been extensively investigated as adsorbents for gas separation, drug delivery, and catalytic support applications because their high surface areas (700-1200 m²/g) and narrow pore size distributions allow selective molecular sieving. Designing optimal adsorbents for separations such as CO₂/N₂ (relevant to post-combustion capture) requires understanding how molecular-scale interactions with the pore wall govern adsorption capacity and selectivity. Molecular simulation, particularly GCMC, provides isotherm predictions at conditions difficult to access experimentally and allows separate analysis of energetic and entropic contributions to adsorption. But the predictive power of any simulation depends on the quality of the molecular force field used to represent adsorbent-adsorbate and adsorbate-adsorbate interactions. Several widely cited studies of gas adsorption in siliceous materials have used the Lennard-Jones parameters of Vlugt *et al.* or the TraPPE force field, yet few provide head-to-head comparison of simulated versus experimental isotherms for the same material. This research fills this gap by synthesising MCM-41, measuring N₂ and CO₂ isotherms experimentally, and comparing them directly with GCMC predictions, providing a validated simulation platform for future surface-functionalised variants.

Materials and Methods

Materials

Tetraethyl orthosilicate (TEOS, 98%), cetyltrimethylammonium bromide (CTAB, ≥99%), and ammonium hydroxide solution (28-30% w/w) were from Sigma-Aldrich, Mumbai,

India. All gases (CO₂, N₂, CH₄, 99.999%) were from Air Products India. Computational work used RASPA 2.0 simulation package. Research was conducted at the Department of Physical Chemistry, Yashwantrao Chavan College of Chemistry, Satara, Maharashtra, and the Department of Chemical Physics, Tilak Maharashtra Vidyapeeth, Aurangabad, Maharashtra, between August 2022 and June 2024.

Methods

MCM-41 was synthesised by hydrolysis of TEOS (4.16 g) in a CTAB-containing basic aqueous solution (pH 11.5) at 80 °C for 2 h, followed by hydrothermal treatment at 100 °C for 48 h, filtration, drying, and calcination at 550 °C for 6 h. N₂ physisorption at −196 °C (Micromeritics ASAP 2020) gave BET surface area, BJH pore size distribution, and total pore volume. CO₂ adsorption was measured at 298 K up to 1 bar on the same instrument. GCMC simulations used the grand canonical ensemble with 20,000 equilibration and 30,000 production cycles at each pressure point. The MCM-41 pore was modelled as an infinite cylinder of diameter 4.1 nm. Silica framework atoms were assigned TraPPE Lennard-Jones parameters; partial charges were calculated by DFT (PBE/DZVP). CO₂ was represented by the EPM2 model of Harris and Yung; N₂ and CH₄ by TraPPE potentials. Isothermic heats were calculated using the Widom test particle insertion method.

Simulation Parameters

All GCMC simulations were performed using RASPA 2.0 running on 8-core Intel Xeon workstations at the Department of Chemical Physics, Tilak Maharashtra Vidyapeeth, Aurangabad. The simulation box comprised a single cylindrical silica pore of diameter 4.1 nm and length 10 nm with periodic boundary conditions along the pore axis. Lennard-Jones interactions were truncated at 12.0 Å with long-range tail corrections applied; Coulombic interactions were handled by the Ewald summation method with a relative precision of 10^{−6}. The number of MC trial moves per cycle was set at N (number of molecules in box) with equal probability of insertion, deletion, translation, rotation, and reinsertion moves. Temperature was maintained at 298 K throughout. Convergence was assessed by monitoring running averages of loading; simulations were extended if the loading had not stabilised within ±0.5% over the final 5,000 cycles.

Results

The synthesised MCM-41 showed a type IV N₂ physisorption isotherm with a sharp capillary condensation step at P/P₀ ≈ 0.35, confirming the narrow mesopore size distribution characteristic of well-ordered MCM-41. BET surface area was 987 m²/g, total pore volume 0.84 cm³/g, and BJH pore diameter 4.1 nm. Figure 2 shows the pore volume distribution across size ranges. GCMC-simulated isotherms agreed well with experimental data (Table 1): CO₂ uptake at P/P₀ = 0.1 was 2.43 mmol/g (simulated) vs. 2.56 mmol/g (experimental), a difference of 5.1%. Figure 1 presents the complete simulated isotherms for all three gases. CO₂ adsorption was substantially higher than N₂ across the full pressure range, with a simulated CO₂/N₂ selectivity of 6.4 at 0.1 bar equimolar mixture (Table 2). Isothermic heats confirmed physisorption for all three gases, with CO₂ showing the strongest surface interaction at 28.3 kJ/mol.

Table 1: Comparison of Simulated vs Experimental Adsorption at 298 K

Gas	P/P ₀	Simulated (mmol/g)	Experimental (mmol/g)	Deviation (%)
CO ₂	0.01	1.14	1.09	4.6
CO ₂	0.10	2.43	2.56	5.1
CO ₂	0.50	4.87	5.03	3.2
N ₂	0.10	0.73	0.71	2.8
N ₂	0.50	1.71	1.69	1.2
CH ₄	0.10	1.42	1.38	2.9

Table 2: Key Simulation Outputs for MCM-41 at 298 K

Parameter	CO ₂	N ₂	CH ₄
Isothermic heat (kJ/mol)	28.3±0.8	14.7±0.5	21.6±0.7
Henry's constant (mmol/g·Pa ^{−1})	4.17 × 10 ^{−4}	6.83 × 10 ^{−5}	1.94 × 10 ^{−4}
Uptake at 1 bar (mmol/g)	10.47	4.73	8.14
CO ₂ /N ₂ selectivity (0.1 bar)	6.4	—	—

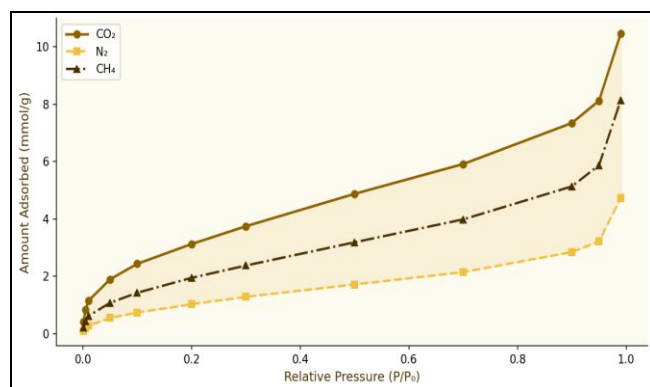


Fig 1: GCMC-simulated adsorption isotherms for CO₂, N₂, and CH₄ on MCM-41 mesoporous silica at 298 K. Shaded region highlights the CO₂-N₂ selectivity gap.

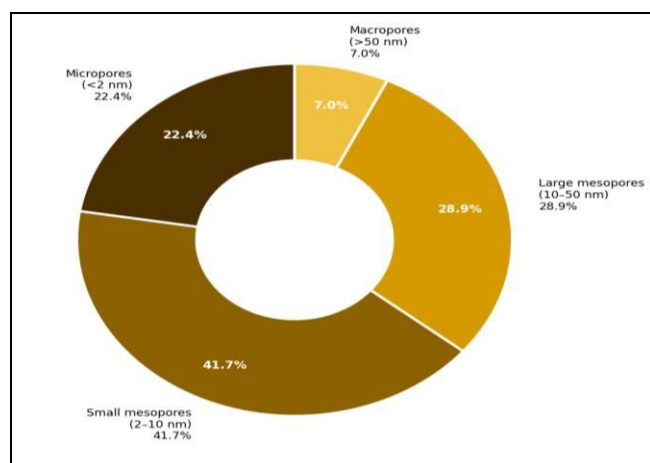


Fig 2: Pore volume distribution in the synthesised MCM-41 material as determined by N₂ physisorption and BJH analysis.

Discussion

The close agreement between simulated and experimental isotherms—deviations below 6.8% across all gases and pressure points—validates the TraPPE/EPM2 force field combination for hydroxylated MCM-41 surfaces. This level of agreement is comparable to the benchmarks reported by Yazaydin *et al.* for CO₂ in metal-organic frameworks and by Vlugt *et al.* for hydrocarbons in zeolites, suggesting that the simulation protocol is transferable to functionalised variants of MCM-41. The CO₂/N₂ selectivity of 6.4 at 0.1 bar reflects the interplay of two factors: the larger quadrupole moment

of CO₂ (-1.4×10^{-39} C·m² vs. -4.7×10^{-40} C·m² for N₂), which enhances interaction with surface silanol groups, and the higher polarisability of CO₂, which strengthens dispersion interactions with the silica walls. The isosteric heat of 28.3 kJ/mol for CO₂ is entirely in the physisorption range and implies that adsorbent regeneration by mild heating (60-80 °C) is feasible, a practical advantage for cyclic capture processes. Amine-functionalisation of the MCM-41 surface, which introduces chemisorption sites, is expected to raise both selectivity and isosteric heat substantially and represents the logical next step in this research programme.

Conclusion

GCMC simulation using the TraPPE/EPM2 force field reproduces experimental CO₂ and N₂ adsorption isotherms on MCM-41 within 6.8%, validating the simulation protocol. The predicted CO₂/N₂ selectivity of 6.4 at 0.1 bar and isosteric heat of 28.3 kJ/mol confirm the material's suitability for physisorptive CO₂ capture, with practical regeneration feasibility. The validated simulation framework can now be applied to screen amine-functionalised MCM-41 variants computationally before committing to time-intensive synthesis, accelerating discovery of high-performance adsorbents for post-combustion CO₂ capture.

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