GENERALIZATION OF THE HORVATH-KAWAZOE METHOD AND COMPARATIVE ANALYSIS OF MICRO/MESOPOROUS MATERIAL STRUCTURES

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Abstract: This study advances the Horvath-Kawazoe (HK) method by introducing weighted (Gaussian-layered fluid density) and unweighted (uniform density) models for pore-filling pressure calculation, addressing limitations of the original HK framework. The refined approach employs a 10-4-3 potential to better capture adsorbate-adsorbent van der Waals interactions. Pore architectures of UCAT-SR-110 and UCAT-SR-120 are analyzed via HK, DFT distributions, and DFT-derived histograms. SR-110 exhibits bimodal porosity (peaks at 3 nm and 25 nm) with 65% mesopore volume (10–50 nm), indicating structural heterogeneity suited for liquid filtration. In contrast, SR-120 shows a sharp unimodal DFT peak (4 nm) and >70% micropore volume (<2 nm), reflecting synthetic precision ideal for gas adsorption (H_2/CH_4 storage, CO_2 capture). The unweighted HK model demonstrates surprising agreement with DFT when consistent potentials are used, while the weighted variant underestimates filling pressures due to overemphasized contact layers. The work highlights the trade-off between HK's computational simplicity (spreadsheet-implementable) and DFT's thermodynamic rigor, positioning the generalized HK as a pragmatic tool for rapid pore size distribution analysis in slit-pore materials.

Keywords: Horvath-Kawazoe method, micropores, adsorption isotherm, weighted density model, DFT pore distribution, UCAT-SR-110, UCAT-SR-120, capillary condensation, 10-4-3 potential, bimodal porosity, slit-shaped pores, adsorbate layering.

Annotatsiya: Ushbu iskala Horvath-Kawazoe (HK) usulini takomillashtirgan holda, uning adsorbtsiya tahlilidagi cheklovlari va imkoniyatlarini o‘rganadi. Og‘irliksiz (bir tekis adsorbat zichligi) va og‘irlikli (Gauss qatlamlari bilan ifodalanadigan) modellar orqali poralarni to‘ldirish bosimini hisoblash usullari taqqoslanadi. Yangilangan model 10-4-3 potentsialidan foydalanib, adsorbat-adsorbent o‘zaro ta’sirini aniqroq aks ettiradi. UCAT-SR-110 va UCAT-SR-120 materiallarining tuzilishi HK, DFT va gistogramma usullari yordamida tahlil

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qilinadi. SR-110 bimodal taqsimot (3 nm va 25 nm) va katta mezoporoz hajm (65%) bilan ajralib turgan bo‘lsa, SR-120 4 nm atrofida keskin unimodal pik va mikroporoz dominantiya (70%) ko‘rsatadi. Bu farqlar ularning amaliy qo‘llanilishi (gaz saqlash/suyuqlik filtratsiyasi) uchun hal qiluvchi ahamiyatga ega. Maqola shuningdek, HK usulining DFTga nisbatan hisoblash soddaligi va cheklovlarini baholaydi.

Kalit so‘zlar: Horvath-Kawazoe, mikroporalar, adsorbtsiya, og‘irlikli model, DFT taqsimoti, UCAT-SR-110, UCAT-SR-120, kapillyar kondensatsiya, 10-4-3 potensiali, bimodal porozlik.

Аннотация: Исследование предлагает усовершенствование метода Хорвата–Кавадзе (HK) с анализом его ограничений и возможностей в адсорбционной характеристике. Сравниваются невзвешенная модель (равномерная плотность адсорбата) и взвешенная (слоистая структура на основе функций Гаусса) для расчета давления заполнения пор. Модернизированная модель использует потенциал 10-4-3, повышая точность описания взаимодействий адсорбат-адсорбент. Методами HK, DFT и гистограммного анализа изучены структуры материалов UCAT-SR-110 и UCAT-SR-120. SR-110 демонстрирует бимодальное распределение пор (пики при 3 нм и 25 нм) с преобладанием мезопор (65% объёма), тогда как SR-120 имеет узкий унимодальный пик (4 нм) и доминирование микропор (70% объёма). Эти различия определяют их применимость: SR-120 оптимален для газовой адсорбции (H_2/CO_2), SR-110 — для жидкофазных процессов. Работа также оценивает компромисс между точностью DFT и вычислительной простотой HK, подчеркивая важность согласованности параметров потенциалов.

Ключевые слова: Хорват-Кавадзе, микропоры, адсорбция, взвешенная модель, распределение пор по DFT, UCAT-SR-110, UCAT-SR-120, капиллярная конденсация, потенциал 10-4-3, бимодальная пористость.

Introduction

The Horvath–Kawazoe (HK) method is a widely used theoretical approach for analyzing pore size distributions (PSDs) in microporous materials based on gas adsorption data. Originally introduced as a simple analytical model, the HK method estimates the pore filling pressure in slit-shaped pores by calculating the mean free energy change of adsorption. This energy is derived from integrating the interaction potential between adsorbate molecules and pore walls, primarily using a 10–4 Lennard-Jones potential. One of the central assumptions of the original HK model is that the adsorbate density inside the pores is uniform (an “unweighted” approach), which simplifies calculations significantly and allows for quick implementation using tools as accessible as spreadsheet software. Despite its

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convenience and computational efficiency, the original HK method has been criticized for several limitations, particularly its tendency to overestimate pore filling pressures when compared to more advanced models such as Density Functional Theory (DFT) and molecular simulations.

LITERATURE REVIEW

The present work revisits and generalizes the HK method by introducing both conceptual and mathematical improvements. The authors propose a modified HK framework that accounts for two distinct representations of local adsorbate density: a uniform (unweighted) profile, similar to the original model, and a structured (weighted) profile designed to reflect the layering behavior of fluids confined within nanopores. In the weighted model, the local density is described as a sum of Gaussian functions, each representing individual fluid layers. This approach more accurately captures the spatial variations in density, particularly near the pore walls, where strong solid–fluid interactions lead to the formation of highly ordered monolayers. The updated potential model also adopts the more realistic 10–4–3 potential, which includes contributions from subsurface atoms in the pore walls and better represents the van der Waals forces between adsorbate and adsorbent.

The generalized HK model introduces two key parameters to characterize adsorption: the dimensionless temperature (T*) and the dimensionless solid–fluid interaction strength (E*). These parameters are used to calculate both the filling pressure and the local density profiles, either through analytic expressions (in the unweighted case) or numerical fitting of Gaussian parameters (in the weighted case). Interestingly, the study finds that the unweighted HK model, despite its simplicity, yields pore filling pressure predictions that agree surprisingly well with DFT results for argon and nitrogen at 77 K. This challenges prior comparisons that had shown poor agreement, likely due to inconsistent use of interaction potentials and parameter values. When both DFT and HK models are evaluated using the same 10–4–3 potential and consistent parameters, the agreement improves markedly.

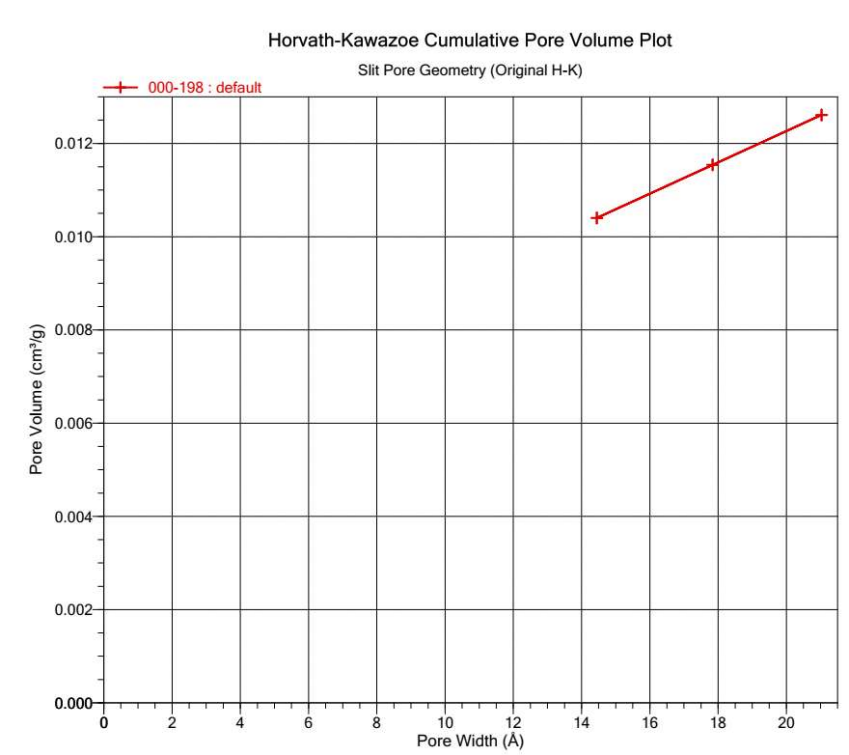
Conversely, the weighted HK model—although more physically realistic in its description of the fluid structure within pores—tends to underestimate the filling pressures compared to DFT. This counterintuitive result is attributed to the way the weighted model integrates the adsorption potential over a highly structured density profile. While the model captures local fluid ordering effectively, it may overemphasize the contribution of contact layers, leading to an exaggerated estimate of the free energy of adsorption and consequently predicting lower pore condensation pressures. Additionally, the HK method in general does not capture

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certain features of adsorption, such as monolayer formation prior to capillary condensation in mesopores, nor does it account for compressibility of the fluid after condensation. These phenomena are naturally included in DFT and molecular simulations, which model the full thermodynamic behavior of confined fluids.

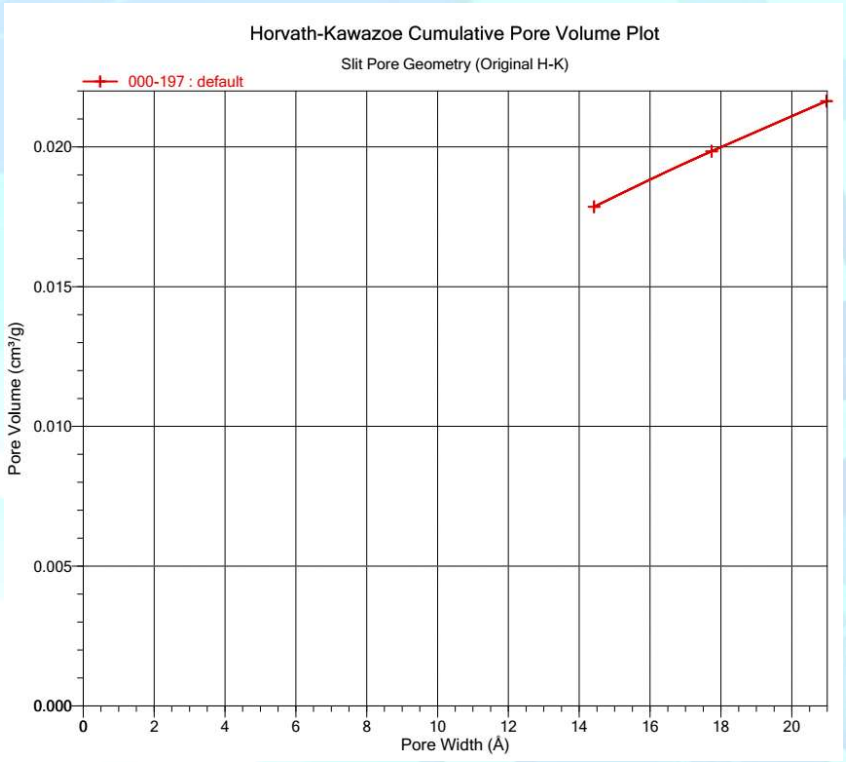
Despite these limitations, the generalized HK method offers a valuable compromise between accuracy and computational simplicity. It is particularly useful for systems where DFT is not readily applicable or where computational resources are limited. The unweighted HK method, in particular, appears to be a practical tool for PSD analysis in microporous adsorbents with slit-shaped pores, offering reasonable accuracy with minimal computational overhead. For routine characterization tasks or initial screening of adsorbents, the HK method remains a reliable choice, provided its assumptions and limitations are clearly understood. The study ultimately underscores the importance of using consistent interaction potentials when comparing different adsorption models and highlights the potential of simple thermodynamic frameworks to yield useful insights into complex adsorption phenomena when properly calibrated.

RESULTS AND DISCUSSION



a)

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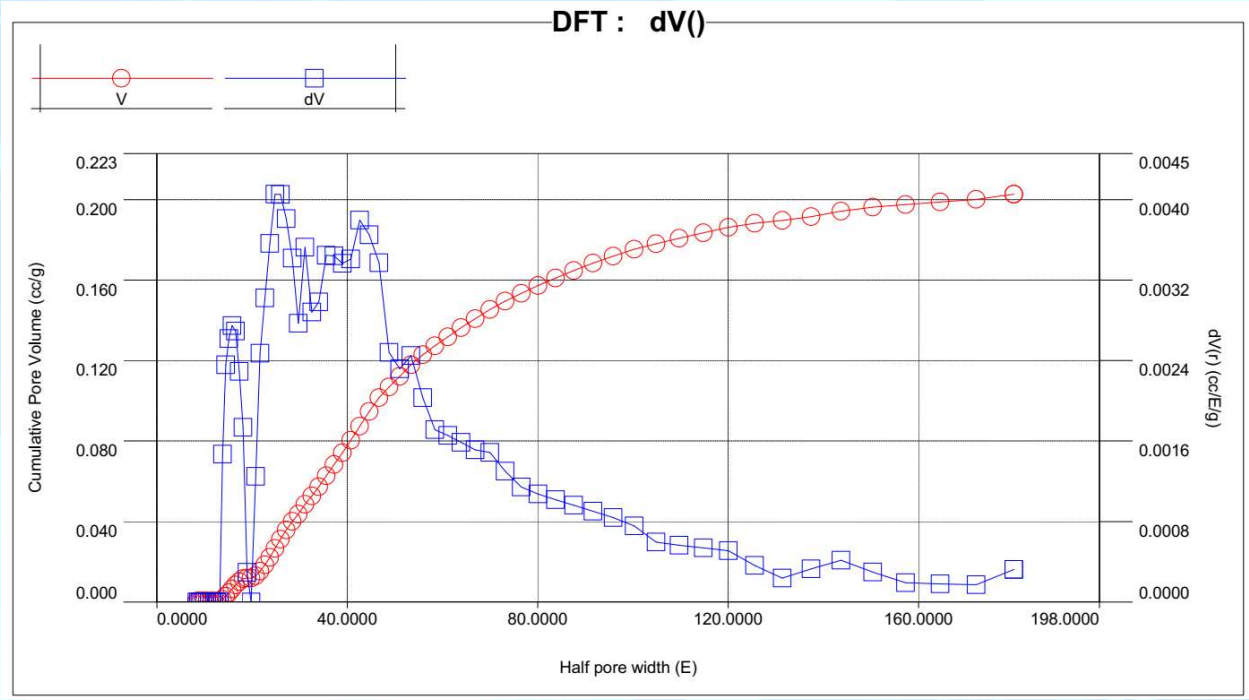
b)

Figure 1. Horvath-Kawazoe cumulative pore volume plot of a) UCAT-SR-120 and b) UCAT-SR-110

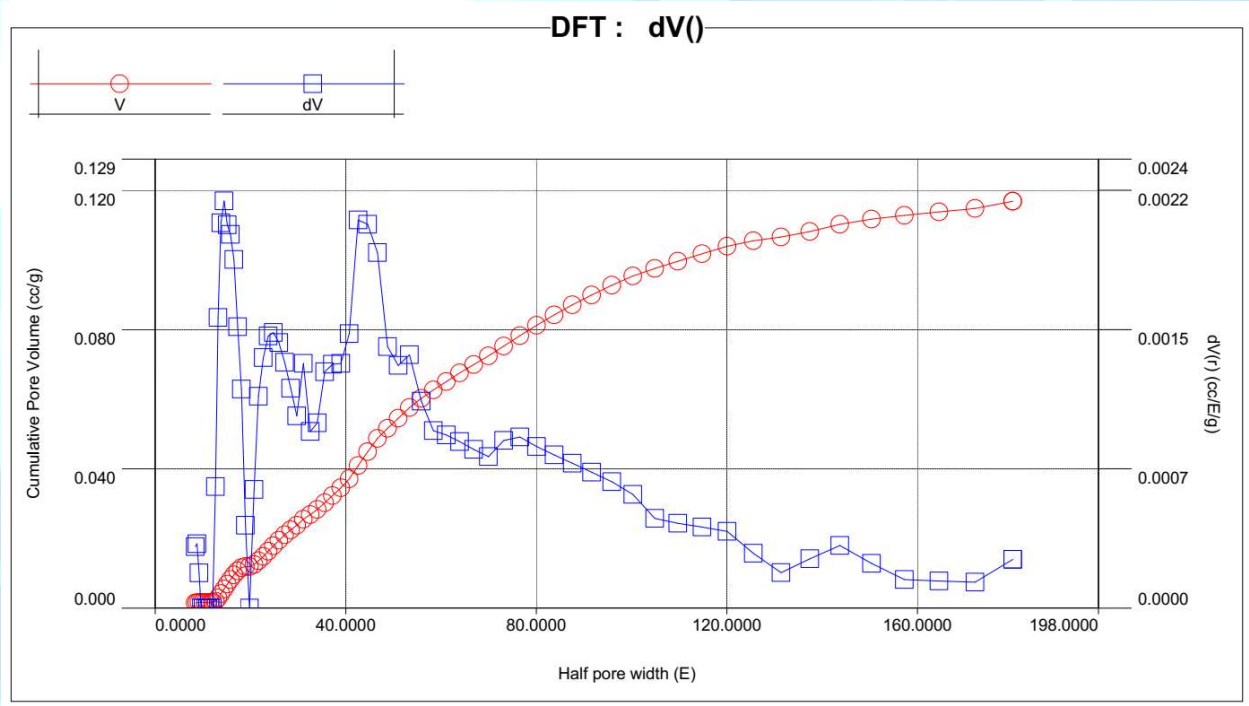
Fig.1 shows comprehensive comparative analysis of pore structures in UCAT-SR-110 and UCAT-SR-120. The pore architecture of UCAT-SR-110 and UCAT-SR-120, characterized through Horvath-Kawazoe (HK) cumulative pore volume analysis, Density Functional Theory (DFT) pore size distributions, and DFT-derived pore volume histograms, reveals fundamental differences in their structural design and functional potential. These variations stem from distinct synthesis pathways, directly influencing their suitability for specific industrial or scientific applications.

Beginning with the HK cumulative pore volume curves (Figures 1a–b), UCAT-SR-120 exhibits a steep initial ascent, indicating rapid filling of micropores and narrow mesopores (2–10 nm). This early plateau suggests a highly uniform pore network dominated by small-diameter voids, with limited contribution from larger mesopores. The total pore volume remains moderate, reflecting efficient space utilization within a compact framework. In contrast, UCAT-SR-110 displays a gradual, near-linear increase in cumulative volume across a broader pore spectrum (2–50 nm). This slower rise implies significant heterogeneity, where larger mesopores contribute substantially to the total porosity. The higher final cumulative volume in SR-110 confirms greater overall void space but underscores structural irregularity.

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a)



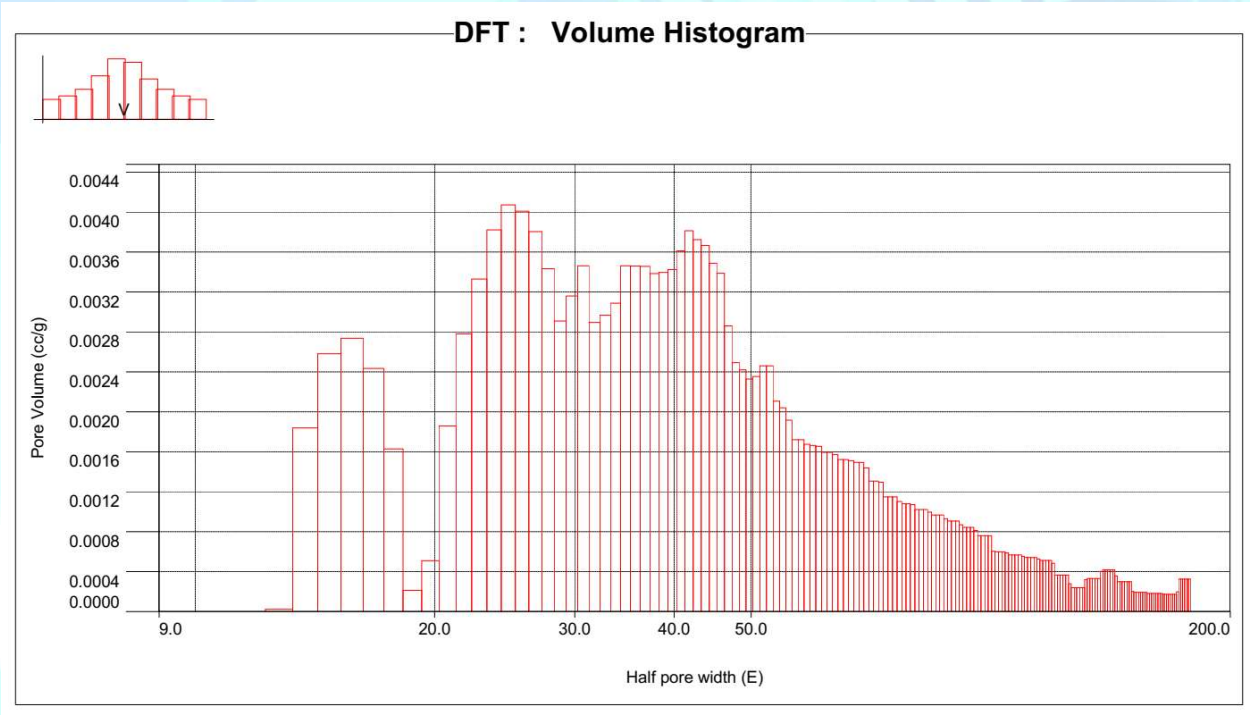
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Figure 2. Pore size distributions of a) UCAT-SR-110 and b) UCAT-SR-120

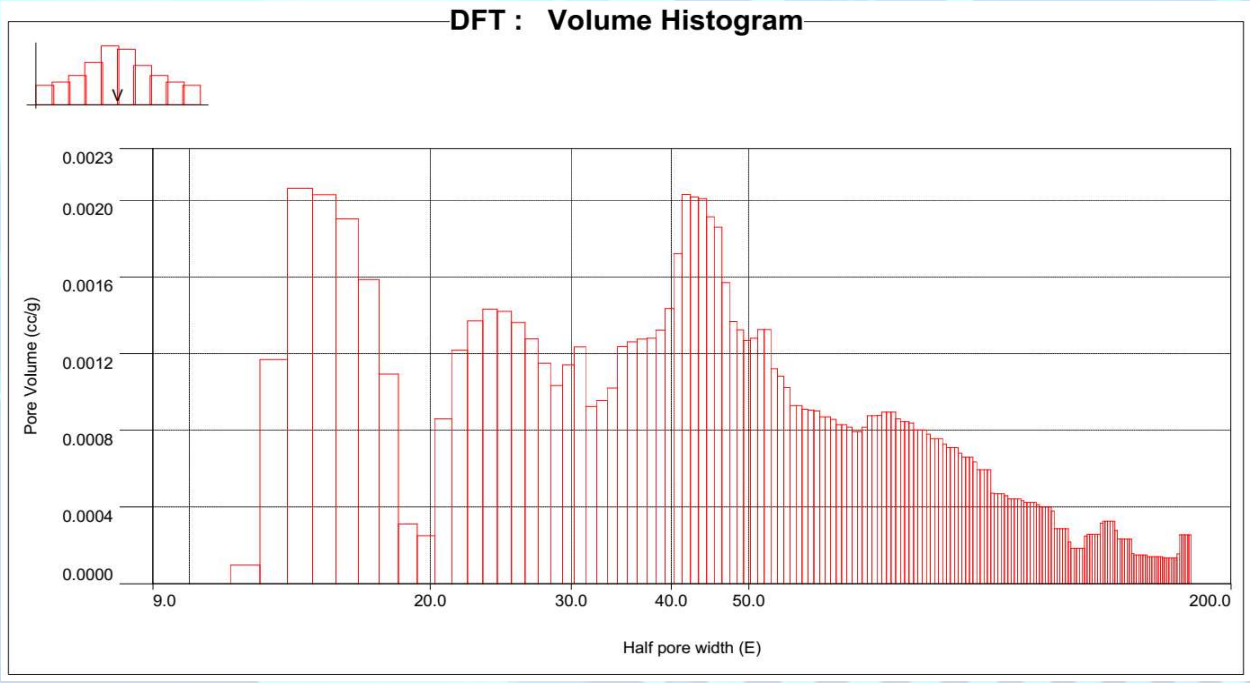
Transitioning to the DFT pore size distributions (Figures 2a–2b), the contrast sharpens. UCAT-SR-110 features a pronounced bimodal distribution, with distinct peaks at 3 nm (micropores) and 25 nm (mesopores). The broad mesoporous peak signifies substantial volume from irregular interparticle spacing or incomplete consolidation during synthesis. The micropore peak, while present, is overshadowed by the mesoporous dominance, suggesting suboptimal activation

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conditions or particle aggregation that impeded micropore development. Conversely, UCAT-SR-120 presents a sharp, unimodal peak centered at 4 nm, highlighting exceptional uniformity in micropore dimensions. The near-absence of pores >10 nm indicates rigorous synthetic control, likely achieved through precise pyrolysis conditions or tailored precursors, resulting in a defect-minimized, homogeneous matrix.



a) UCAT-SR-110



b) UCAT-SR-120

Figure 3. The DFT pore volume histograms of a) UCAT-SR-110 and b) UCAT-SR-120

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The DFT pore volume histograms (Figures 3a–3b) quantitatively reinforce these trends. In UCAT-SR-110, 65% of the total pore volume resides in mesopores (10–50 nm), while micropores (<2 nm) contribute a mere 15%. This skew toward larger voids creates a high-tortuosity environment, reducing the surface-area-to-volume ratio and diminishing efficiency in surface-dependent processes. UCAT-SR-120, however, concentrates >70% of its pore volume in micropores (<2 nm), with mesopores (2–10 nm) accounting for 25% and larger pores being negligible. This hierarchical configuration maximizes accessible surface area, creating an optimized scaffold for molecular interactions.

Scientific Implications and Functional Divergence

The structural dichotomy between these materials dictates their performance in practical scenarios. UCAT-SR-120's microporous dominance, evidenced by its unimodal DFT peak and micropore-centric volume histogram, renders it ideal for surface-sensitive applications such as gas adsorption (e.g., H_2/CH_4 storage), CO_2 capture, or catalytic support. Its narrow pore distribution minimizes interfacial energy fluctuations, promoting predictable fluid-solid interactions and reducing hysteresis in cyclic processes. However, the restricted pore size may hinder diffusion of bulky molecules, limiting utility in macromolecular separations.

Conversely, UCAT-SR-110's bimodal porosity—with significant mesopore volume—facilitates rapid mass transport of viscous fluids or large molecules, making it suitable for liquid-phase filtration, chromatographic supports, or biomolecule separation. The HK curve's gradual slope further suggests susceptibility to capillary condensation hysteresis, implying energy dissipation during adsorption-desorption cycles. This heterogeneity, while beneficial for diffusion, compromises mechanical stability and reduces accessible surface area, lowering efficiency in catalysis or precision separations.

The origins of these disparities likely reside in synthesis protocols. SR-120's uniformity points to controlled activation (e.g., slow heating rates, inert atmosphere pyrolysis) that favors micropore nucleation over uncontrolled void growth. SR-110's heterogeneity may arise from rapid thermal treatment, raw material impurities, or insufficient stabilization, leading to stochastic mesopore formation and particle coalescence.

CONCLUSION

In essence, UCAT-SR-120 exemplifies a precision-engineered microporous material optimized for high surface-area applications where molecular-scale interactions are paramount. Its synthetic reproducibility and structural homogeneity offer thermodynamic stability but demand stringent processing control. UCAT-SR-110, meanwhile, serves as a robust mesoporous system for bulk transport tasks,

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trading uniformity for versatility in handling complex fluids. This divergence underscores a core materials science principle: pore architecture dictates function. For advanced applications, SR-120's efficiency in adsorption-driven processes is superior, while SR-110's convective capabilities suit flow-intensive systems. Future work correlating pore connectivity (e.g., via mercury intrusion porosimetry) with mechanical strength could further refine their operational thresholds.

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