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The hysteretic behavior in adsorption isotherm of microporous adsorbents: A case study on $Zn(NH_3)(CO_3)$

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Hysteresis associated with capillary condensation is commonly reported for mesoporous materials; in contrast, microporous materials typically show a Type I isotherm as a result of pore filling at low pressures and the leveling off of uptake at higher pressures because of limited accessible pore volume. Nonetheless, hysteresis occasionally has been reported for microporous materials, and such results have been evaluated and interpreted case-by-case rather than justified by common rules like fluid or structure phase transformation. For instance, $Zn(NH_3)(CO_3)$ – a microporous adsorbent with 1-dimentional channels – exhibits H3- or H_4-type hysteresis in the isotherms of CO_2, N_2, H_2, O_2, and CH4 adsorptions at a temperature range from 253 K to 293 K. The hysteresis are attributed to a dual-mode, diffusion-controlled adsorption-desorption. The evaluation of adsorption isotherms of those materials at varied temperatures reveals an exceptional behavior: at least in a limited temperature range, the uptake capacities of such adsorbents are comparatively insensitive to temperature. Surprisingly, it is occasionally observed that the uptake capacity has increased as temperature increased – the opposite functionality with temperature compared with that of ordinary adsorbents. The hysteresis's width and type of those materials, on the other hand, change with temperature. Moreover, a transitional temperature can be found above which the adsorbent experiences abrupt changes in the adsorption capacity and type of hysteresis. All abovementioned characteristics are shown for CO_2 and N_2 adsorption isotherms of proposed case study adsorbent, $Zn(NH_3)(CO_3)$, in the figure. Focusing on the adsorptive behavior of $Zn(NH_3)(CO_3)$, this study aims to explain the hysteretic observance of the isotherms of microporous adsorbents at varied temperatures. The study concludes that significance of resistance against diffusion of adsorptives to the micropores in such materials and adverse functionality of this resistance with temperature in comparison with adsorptive resistance are the origin of such exceptional performance.

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