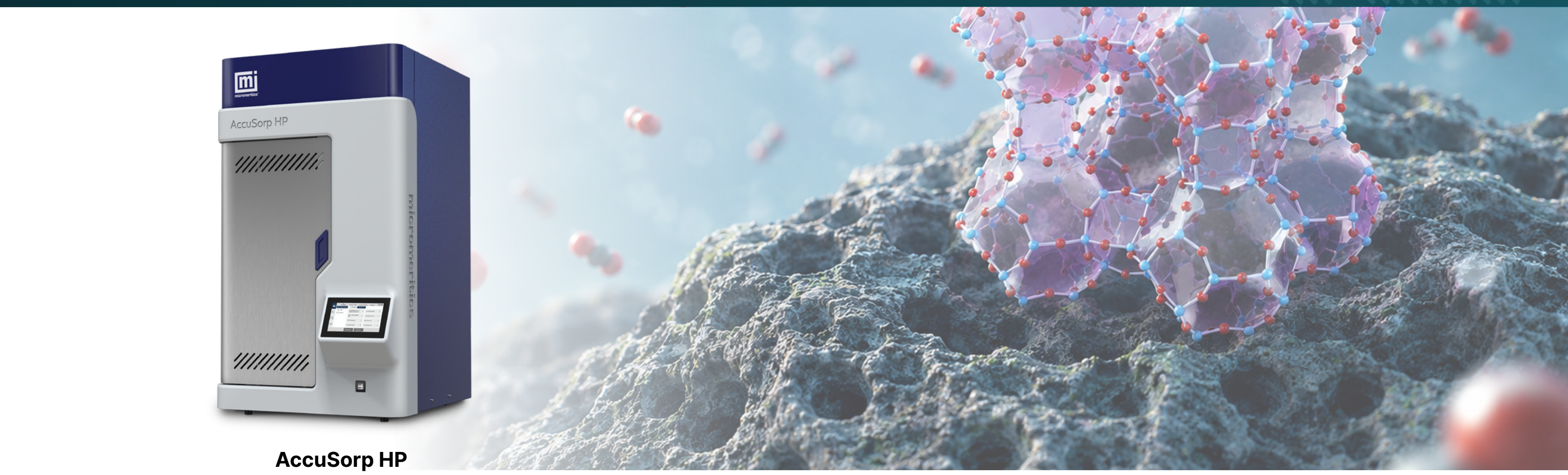
Collecting High Pressure Carbon Dioxide Adsorption Data on the AccuSorb HP: An Analysis of Zeolite and Carbon Materials



AccuSorp HP

Introduction

Carbon capture and storage (CCS) remains a critical area of scientific research as the impacts of climate change are observed globally each year. A primary driver of global warming is the increasing concentration of carbon dioxide in the atmosphere, which has risen steadily since the onset of global industrialization, primarily resulting from the combustion of fossil fuels. Underscoring the urgency of this trend, the World Meteorological Organization reports that the past 11 years have comprised the warmest on record, with continued warming likely heading into the future (wmo.int). In response, research efforts have focused on developing advanced materials to mitigate emissions by capturing carbon dioxide both directly from ambient air as well as from emission point-sources. For these mitigation strategies to be fully realized, efficient capture must be accompanied by secure storage of carbon dioxide.

Multiple pathways exist for the subsequent storage and utilization of captured carbon dioxide. Sequestration strategies include injection into depleted oil and natural gas reservoirs, mineralization within deep geological rock formations, and utilization of carbon dioxide as a feedstock for the production of value-added products. Regardless of the targeted pathway, a comprehensive understanding of the porous materials engineered to store carbon dioxide under elevated pressures is critical.

In this study, the AccuSorp HP was utilized to evaluate high-pressure carbon dioxide adsorption isotherms across a diverse suite of materials, including zeolite 4A, zeolite 5A, zeolite 13X, and a commercial activated carbon from Supelco. This work establishes a framework for collecting high-pressure carbon dioxide adsorption data utilizing the advanced capabilities of the AccuSorp HP.

Experimental

In this work, CO_2 adsorption isotherms were collected on the AccuSorp HP for zeolite 4A, zeolite 5A, zeolite 13X, and Supelco carbon. These isotherms were collected at three temperatures: 15, 25, and 35 ˚C and analyzed up to a maximum pressure of 45 bar. A maximum pressure of 45 bar was chosen for these analyses as the saturation pressure of CO_2 is roughly 50 bar at 15 ˚C, the AccuSorp HP can operate up to a maximum pressure of 200 bar for non-condensable fluids. Limiting the maximum pressure ensured that no condensation would occur within the sample tubes. The AccuSorp HP software will prevent users from analyzing gases at pressures up to or above the saturation pressure, removing the requirement for users to search for the saturation pressure of any gas at their chosen analysis temperature.

Prior to analysis, samples were degassed ex-situ using a VacPrep. All tested samples were degassed at 300 ˚C for 8 hours, as they exhibited high thermal stability and structural degradation upon heating was not a concern. The samples were then transferred to the AccuSorp HP for analysis. The sample holder used consisted of a 2 mL stainless steel sample holder.

To maintain the analysis temperature, an iso controller was set to temperatures of 15, 25, or 35 ˚C for the respective analyses. To obtain the appropriate adsorbed quantity, blank corrections were used as CO_2 deviates significantly from ideal gas behavior especially at high pressure.

Table 1: Analysis Conditions for the CO_2 Adsorption Analyses

Adsorptive Gas	CO_2	
Analysis Temperature	298.15K	
Free Space Type	Measure Before	
Temperature Control	Circulating Bath	
Absolute Tolerance	5 mbar	
Relative Tolerance	5%	
Min Pressure Equilibration Time	60 s	
Max Pressure Equilibration Time	99999 s	
Pressure Increment (bar)	**Equilibration Interval (s)**	**Pressure (bar)**
0.3	60	1
1	60	10
5	60	40
	60	45

Results and Discussion

Adsorption Isotherms

Carbon dioxide adsorption isotherms were collected on the four materials: zeolite 4A, zeolite 5A, zeolite 13X, and Supelco carbon. The collected isotherm data is shown below in Figures 1-4 for measurements collected at 15, 25, and 35 ˚C.

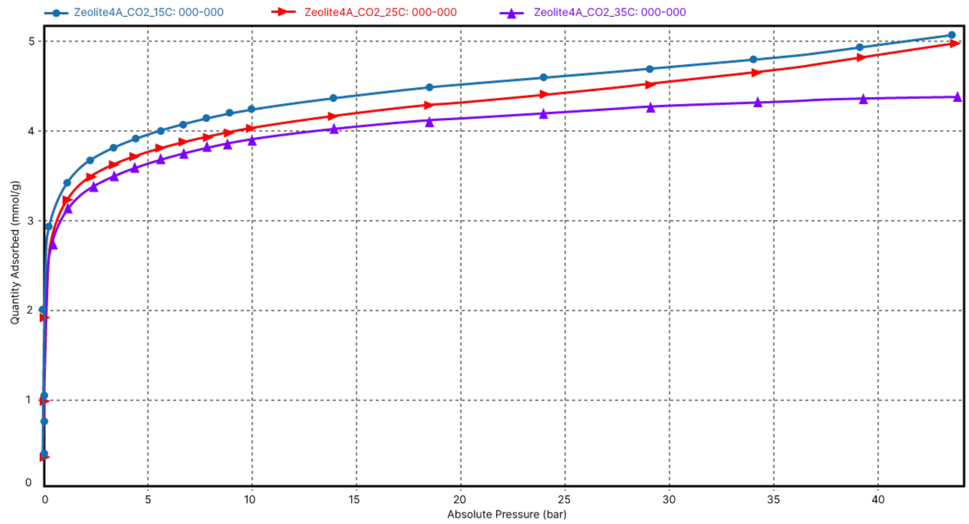


Figure 1: Zeolite 4A CO2 Adsorption Isotherms Collected on the AccuSorp HP up to 45 bar Pressure

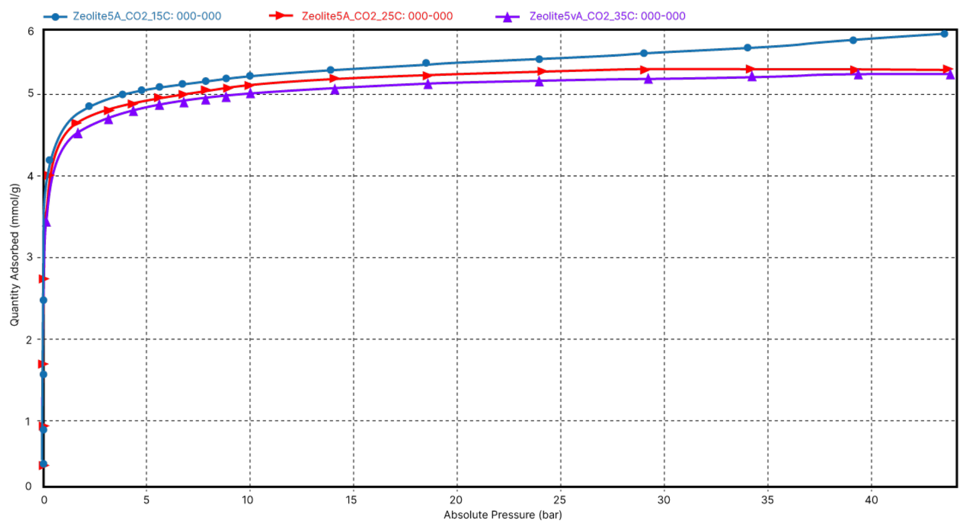


Figure 2: Zeolite 5A CO2 Adsorption Isotherms Collected on the AccuSorp HP up to 45 bar Pressure

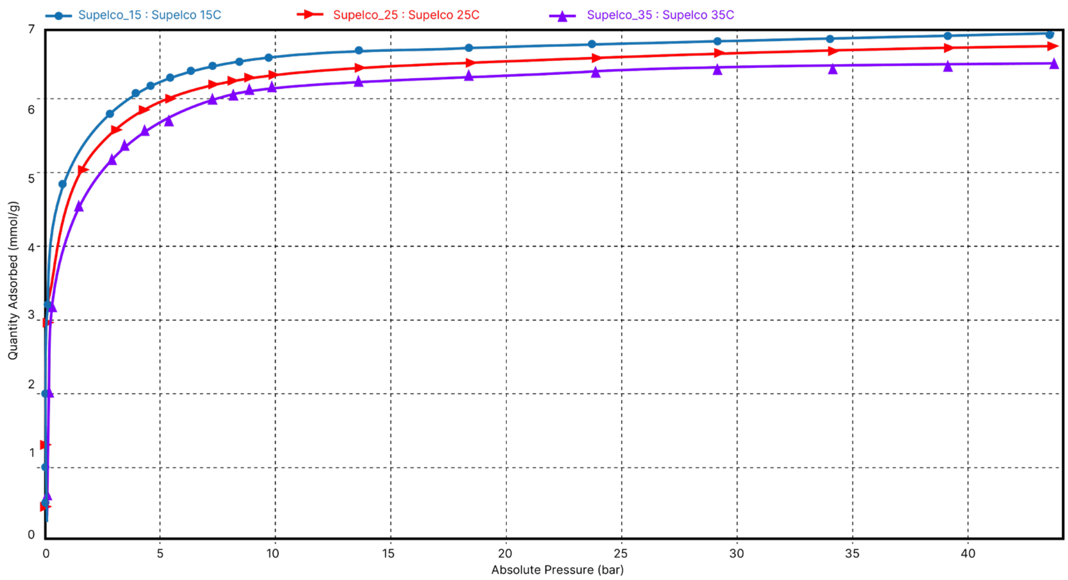


Figure 3: Zeolite 13X CO_2 Adsorption Isotherms Collected on the AccuSorp HP up to 45 bar Pressure

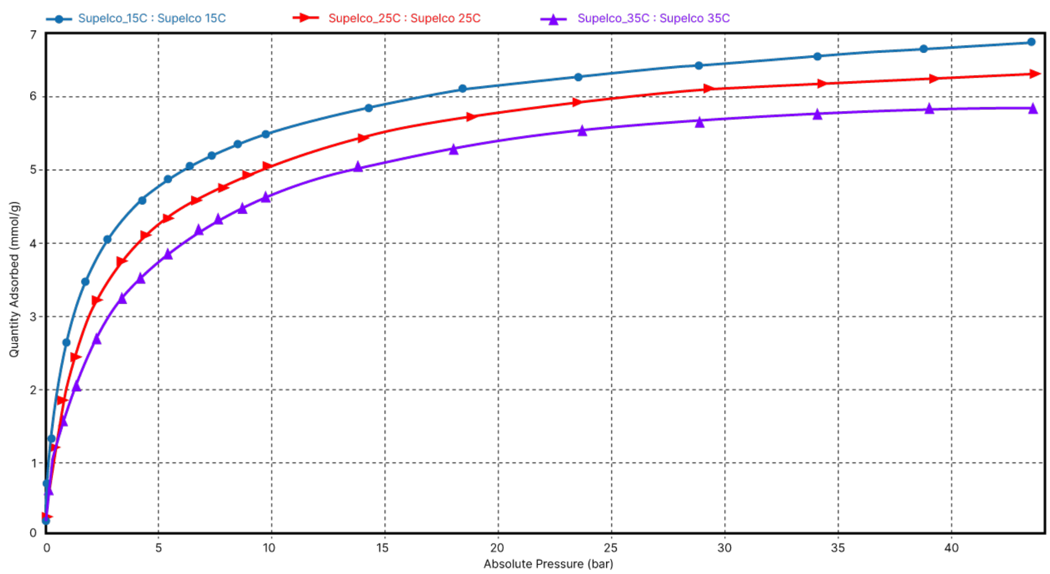


Figure 4: Supelco Carbon CO_2 Adsorption Isotherms Collected on the AccuSorp HP up to 45 bar Pressure

Across all samples, the expected trend of decreasing adsorption capacity with increasing temperature was observed. For the three zeolite samples, strong adsorption was present at low temperatures as expected of highly microporous samples. The Supelco carbon showed lower CO_2 adsorption at low pressure, but excellent capacity once higher pressures were achieved. When comparing the samples at 1 bar of pressure, the zeolite 13X displays the strongest CO_2 adsorption followed by zeolite 5A, then zeolite 4A, and lastly Supelco carbon. At a pressure of 45 bar, zeolite 13X maintains the highest capacity, followed closely by Supelco carbon, then zeolite 5A, and lastly zeolite 4A.

The takeaway from these isotherm measurements is that low pressure adsorption is primarily dominated by adsorption of CO_2 within the smallest pores of the material. At high pressure, the maximum adsorption is primarily driven by the total pore volume of the material. Zeolites 4A and 5A have very small pores that facilitate strong adsorption at low pressure but lack the total volume when compared to zeolite 13X and Supelco carbon. For this reason, these materials completely fill the pore volume quickly and at relatively low pressures.

Heat of Adsorption Reporting

The collected isothermal data from the AccuSorp HP integrates with the MicroActive software suite, enabling heat of adsorption reporting. This allows users to evaluate heat of adsorption of their materials across the range of adsorption coverages. Heat of adsorption is the amount of energy that is released upon adsorption of the adsorbing molecule onto the surface of a material. Higher numbers indicate a stronger interaction. Figure 5 below shows the calculated heats of adsorption for the four materials analyzed in this study.

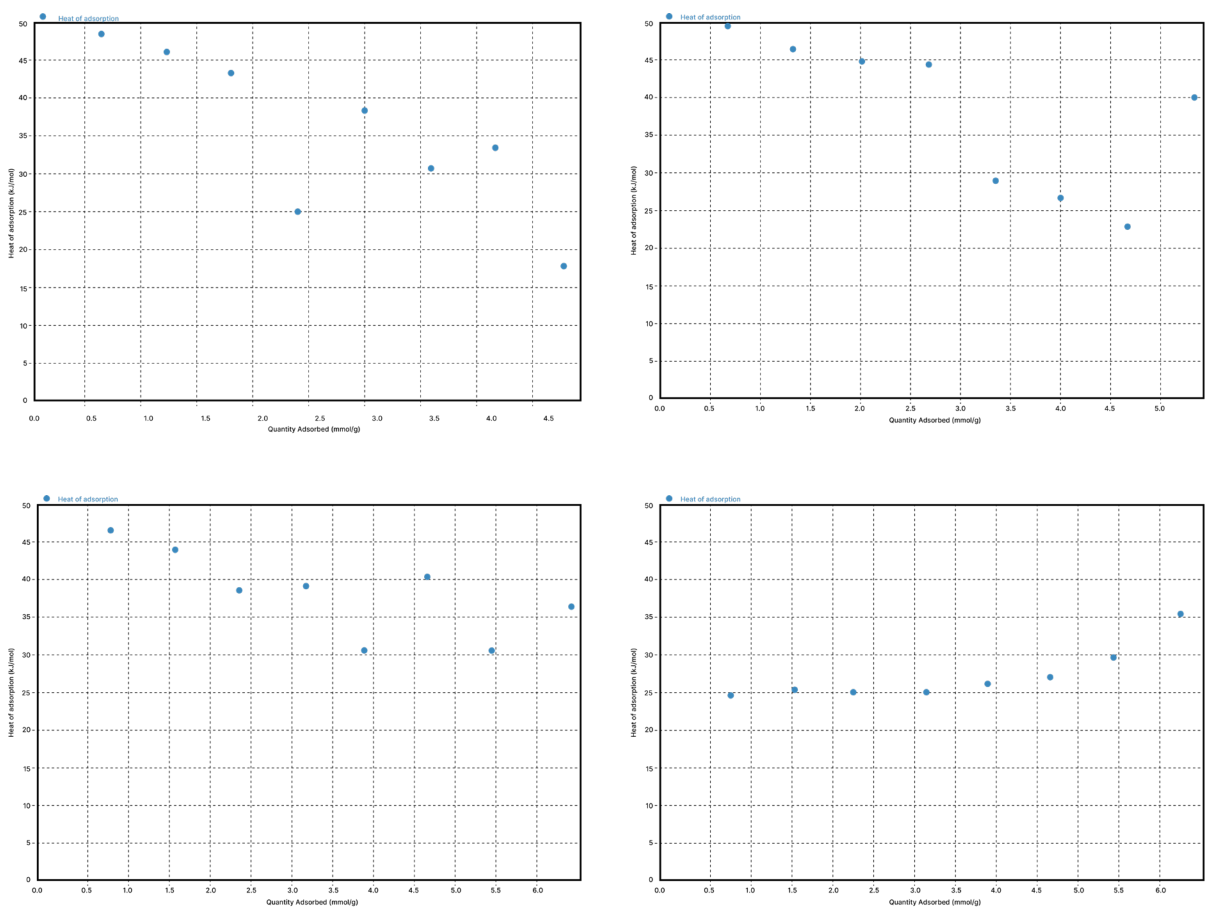


Figure 5: CO_2 Heat of adsorption plots for zeolite 4A (top left), zeolite 5A (top right), zeolite 13X (bottom left), and Supelco carbon (bottom right)

The results from the heat of adsorption report are consistent with earlier observations from the isothermal data that was obtained on the zeolite and carbon materials. The three zeolite materials display large heats of adsorption, nearly 50 kJ/mol at zero coverage, which decreases at increasing coverage. The loss in heat of adsorption energy with decreasing coverage is most pronounced for the zeolite 4A and zeolite 5A materials. In comparison, the Supelco carbon exhibits a significantly lower heat of adsorption compared to the zeolite materials at zero coverage; however, it remained stable with increasing coverage, maintaining a value near 25 kJ/mol.

Conclusion

This application note provides an overview of high-pressure carbon dioxide adsorption characterization using the AccuSorp HP. Comparative adsorption evaluations were conducted across zeolite 4A, zeolite 5A, zeolite 13X, and a commercial Supelco activated carbon. The zeolites exhibited strong affinity for carbon dioxide adsorption as was evident from their high isosteric heats of adsorption within the range of 45 to 50 kJ/mol at low surface coverage. The Supelco carbon and zeolite 13X both displayed excellent high pressure adsorption of carbon dioxide reaching capacities near 7 mmol/g at the maximum evaluated pressure of 45 bar.

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