Thorough characterizations of micropores with CO_2 adsorption at 195 K

Introduction

Sorption experiments with CO_2 are a widespread method for the characterization of carbon-based and other materials with an emphasis on micropores due to their relevance for climate research. Until now, the most common application was CO_2 sorption at 273 K. The advantages compared to N_2 or Ar measurements are listed as follows:

- Faster analysis times due to a more rapid equilibration at 273 K as opposed to 77 K (N_2) or 87 K (Ar). Typically, the analysis duration is 1/10 of comparable N_2- or Ar sorption experiments. This is especially attractive for quality control or a fast screening of samples.
- Experiments can be conducted without the need for turbomolecular vacuum and its respective sensors for low pressure ranges.
- Penetration of smaller micropores by CO_2 due to a lower critical molecular diameter of 0.28 nm compared to 0.3 nm of N_2.
- Experiments are easier to conduct due to the use of ice water or simple recirculating chiller baths instead of liquid nitrogen.
- No kinetic hinderance on gas diffusion at pore apertures below 0.5 nm, which commonly leads to problems with N_2-adsorption in ultramicropores at 77 K. For example, N_2 does not diffuse into the 0.4 nm-pores of Zeolite 4A even though the critical diameter of the N_2 molecule is well below 0.4 nm. CO_2 adsorption achieves full pore filling below 0.3 nm due to the higher analysis temperature.

As CO_2 has a very high saturation pressure at 273 K of 3,485 kPa, a standard physisorption instrument can only reach relative pressures below 0.03, meaning that only pores below a diameter of 1.5 nm can be resolved. In order to make the pore size range above 2 nm accessible, either a high-pressure instrument is required or the analysis temperature needs to be decreased thus lowering the saturation pressure.

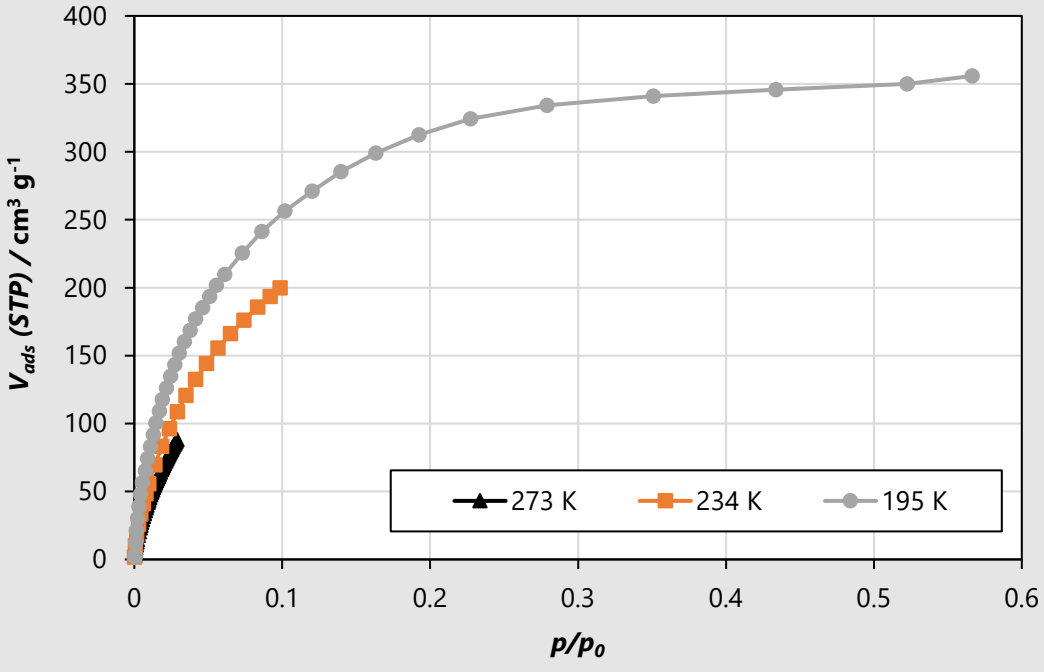

Figure 1 *CO_2-Isotherm of the activated carbon „AC–reference" at 195 K, 234 K and 273 K up to 101 kPa*

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CO_2 experiments

In this article, we will present sorption experiments on an activated carbon conducted at low temperatures and on a simple sorption analyzer without expensive turbo-pump modules and sensor packages (3P Sync 220A). Our focus here to achieve good resolutions of the micropore range with a mere 1,000 mmHg pressure sensor of a standard BET analyzer. Fig. 1 shows CO_2 sorption isotherms at 195 K, 234 K and 273 K on a homogenous activated carbon, which is used as an internal reference material for micropores at 3P Instruments (designated „AC-reference"). Fig. 2 and 3 show the comparison of NLDFT and Monte-Carlo calculations of Ar (at 87 K) and CO_2 sorption (at 273 K) on the same sample. While CO_2 isotherms at 273 K do not fully resolve the complete micro pore range, there is an additional issue of significant discrepancies between the calculated pore size distributions. Even below 1.5 nm, the calculated micropore sizes are strongly undervalued in comparison to the calculations from Ar isotherms.

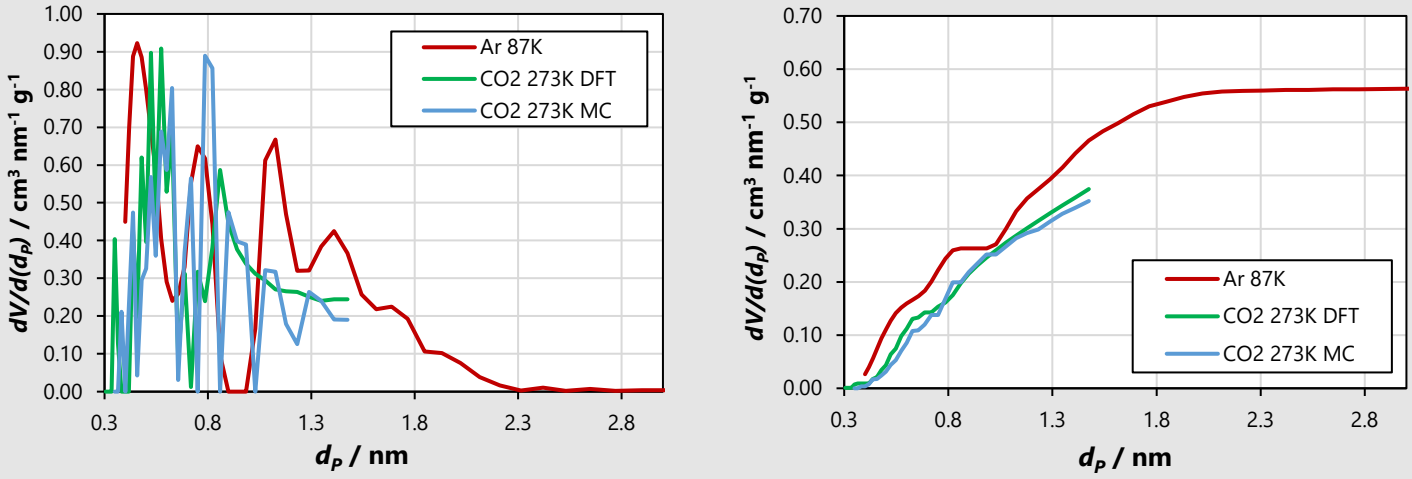
Experimental setup

The question thus is, why CO_2 experiments are rarely carried out at 195 K, if they allow the reliable characterization of pores above 1.5 nm in many materials, especially activated carbons.

Ar- and N_2-based experiments have shown that activated carbons exhibit a wide micropore range up to 2 nm. It is easy to realize that the analysis at 195 K terminates in an adsorption plateau, meaning all available micropores are filled completely. The calculation of micropore sizes by the Horvath-Kawazoe method shows a good accordance of the CO_2-sorption data with the calculation from the Ar-based data.

Fig. 4 shows that results obtained from Ar 87 K, CO_2 195 K and N_2 77 K are in good accordance both quantitatively and qualitatively with each other. It can be put in context with the calculations from NLDFT or Monte-Carlo for CO_2 273 K (see Fig. 2 and 3) as only these models are available for the temperature of 273 K.

Pores with a diameter of up to 5 nm can be completely filled with CO_2-measurements at 195 K. Until now, the temperature of 195 K could only be maintained for short periods of time with dry-ice mixtures or with a compressor-based module called cryoCooler. The cryoTune series from 3P Instruments now finally allows for realizing alternative temperatures within a range 82 K to 323 K.



Figures 2 and 3 *Differential and cumulative comparison between NLDFT (left) and Monte-Carlo-Simulation (right) for the activated carbon „AC-reference".*

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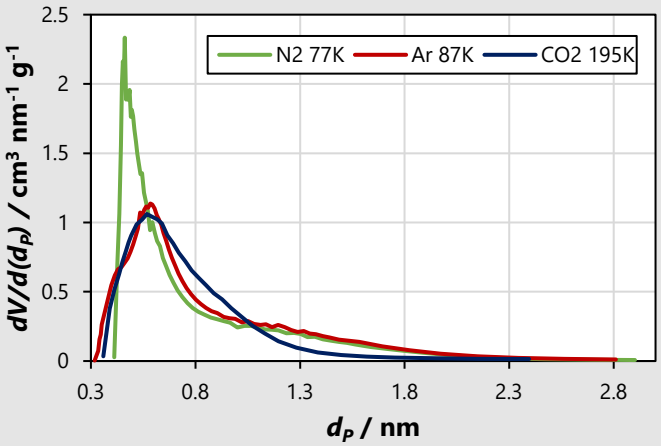

Figure 4 *Horvath-Kawazoe (HK)-calculation of the activated carbon „AC-reference"*

Figure 5 *cryoTune-Setup on a 3P sync*

Table 1 *Parameters used and calculated BET surface area & pore volumes for the activated carbon "AC-reference"*

	CO_2 195 K	CO_2 234 K	CO_2 273 K	Ar 87 K
Liquid density / g cm^{-3}	1.258	1.177	1.096	1.400
Area occupied / nm^2	0.164	0.172	0.179	0.142
BET surface area / m^2 g^{-1}	1,278	1,092	1,077	1,458
Pore volume / cm^3 g^{-1}	0.553	0.335	0.166	0.569 (at p/p_0 = 0.55)
Fraction pore filling / %	97.2	58.9	29.2	100

Fig. 5 depicts the cryoTune 195, which is fitted neatly to a 3P Sync sorption analyzer in its own dewar to the left of the instrument and running completely quiet. The cryoTune series is fitted with different temperature modules allowing the ranges of 82 – 135 K, 115 – 230 K und 180 – 323 K.

Results

In Tab. 1 the textural data calculated from the three experiments conducted with CO_2 are compared to the results from the Argon measurements at 87 K. It shows that merely 30 % of all micropores are filled with CO_2 at 273 K, while this value increases at 234 K to 59 % and the pore system is almost completely filled at 195 K. It has to be assumed that small deviations from the results of the Argon analysis are due to the small uncertainties within the adsorbate parameters. The cryoTune series offers extensive possibilities for advanced material studies with regards to temperature-dependent adsorbate properties.

By implication, this also means that CO_2 sorption analysis at 273 K only leads to limited results for many activated carbons and other materials. Thus, the cryoTune allows for a seamless accessibility of the temperature ranges from 82 K up to room temperature for interesting sorption studies, while at the same time allowing the IUPAC and ISO conform analysis of Ar sorption at 87 K.

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