

How to characterize smallest ultramicropores?

Characterization of
particles • powders • pores

Introduction

Quite often there is a request to decide for a new instrument or a measuring routine to characterize pores larger than 0.35 nm. Independent of the fact that 0.3 nm is the critical and 0.35 nm the so-called kinetic molecule diameter of N₂, there is an illusion that micropores in the range of 0.4 nm might be characterized by the use of N₂ at 78 K. Over the last few years, we have measured numerous ultramicroporous materials. These materials always showed the same characteristics, namely that N₂ is adsorbed at 78 K only by pore sizes larger than 0.5 nm. We employed long-term sorption measurements on a narrow pore Zeolite 4A and explain the effect and possible solutions for the characterization of ultramicropores.

The drying capacity of Zeolite 4A highlights that water molecules with a critical molecular diameter of 0.26 nm at ambient temperature can easily penetrate the pores of the Zeolite 4A, but also the smaller molecules such as N₂, O₂ or CO₂. However, how does that fact explain the incredibly small N₂ adsorption at 78 K in Fig. 1 in comparison to the much larger amounts of H₂ at 78 K and of CO₂ at 195 K?

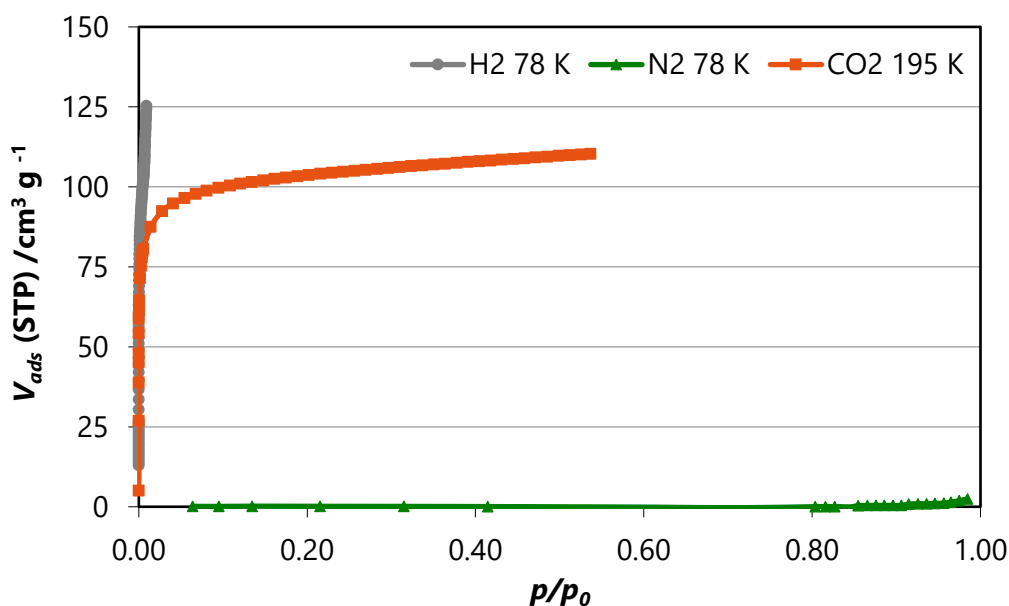


Figure 1 Zeolite 4A isotherms of H₂ at 78 K, CO₂ at 195 K, and N₂ at 78 K

Almost no N₂ adsorption at 78 K, but a very pronounced adsorption at room temperature poses the question, how the adsorption behavior looks in the range of temperatures between these two extreme points and which conclusions can be drawn from the data. In order to gain some answers, special N₂ physisorption experiments were conducted over a broad temperature range.

Experimental

After sample preparation of the Zeolite 4A, the following experiments were carried out in the following order by use of a sorption analyzer with a cryoCooler: Firstly, only one point at 101 kPa was chosen for all selected temperatures, since we focused on the temperature dependent uptake of the analysis gas and long analysis times were expected. Furthermore, in each measurement the absolute possible maximum of adsorptive molecules was provided, in order to minimize the probability for molecules hitting the pore apertures.

How to characterize smallest ultramicropores?

Characterization of
particles • powders • pores

The instrument reached the desired pressures, but in the case of significant adsorption (and falling pressures) a redosing was carried out to hold constant 101 kPa as equilibrium pressure. Equilibrium conditions were set to constant 48 hours for each temperature. The analysis data were evaluated using the constantly running log-file in parallel to the measurement. According to this procedure, the maximum amount of adsorbed nitrogen was determined at 101 kPa for temperatures between 78 K and 150 K (see Fig. 2).

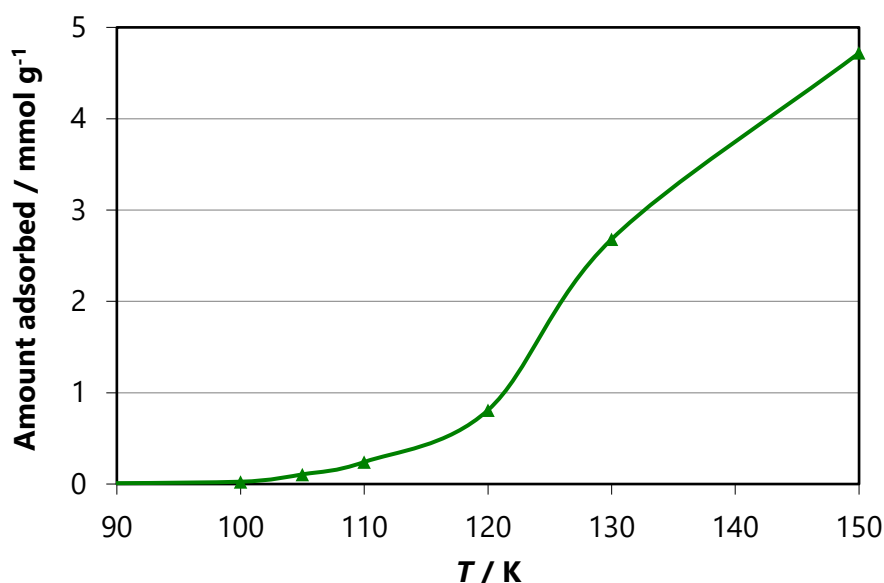


Figure 2 Volume adsorbed of N_2 at different temperatures in the pore system of Zeolite 4A after 48 h equilibration time for each measuring point

Results and Discussion

With a critical N_2 molecule diameter of 0.30 nm, these molecules should be able to penetrate the 0.4 nm pores of a Zeolite 4A and be adsorbed. And, from a thermodynamic point of view at constant pressure, the amount adsorbed increases with decreasing temperature. However, Fig. 2 shows clearly the thermodynamically unexpected behavior of the N_2 adsorption. We find the opposite for 0.4 nm pore diameters in a special temperature range: the higher the temperature, the higher the volume adsorbed. Even for a very long equilibration time of 48 h per recorded analysis point, it is impossible to assume a complete equilibration of the adsorption measurement. The uptake presents itself as a kinetically hindered adsorption process. In the temperature range between 150 K and 100 K, the adsorbed amount falls to very low values. However, this decrease is not abrupt and does not reach zero at a clearly defined fixed temperature.

Tab. 1 illustrates that the nitrogen adsorption on Zeolite 4A is not caused by a sieving effect, but is kinetically hindered below a temperature of 150 K and extremely hindered below 110 K. The results lead us to the conclusion that N_2 molecules can enter into the outer pores of the zeolite particles and diffuse further into the pore system over the course of 48 h. This diffusion process is strongly hindered and highly dependent on temperature, which means that at 100 K only very small amounts of diffusion into the micropore system can be observed.

How to characterize smallest ultramicropores?

Characterization of
particles • powders • pores

Table 1 N_2 adsorption at 78 K in Zeolite 4A after 48 h equilibration

Temperature / K	Amount adsorbed / $mmol\ g^{-1}$
100	0.03
110	0.24
130	2.68
150	4.72

A similar example is demonstrated in Fig. 3 showing two samples on the basis of charcoal. Sample A has a little higher CO_2 adsorption at higher measuring temperatures and its N_2 78 K isotherm shows a similar adsorption behavior with respect to CO_2 at 273 K. In contrast to that, the ultramicropores of sample B are too small for an unhindered diffusion process at 78 K. Only the adsorption at higher temperatures is usable for such ultramicroporous materials, and CO_2 adsorption at 273 K, but especially at 195 K to reach a complete micropore filling and BET-range (see Fig. 2), is the right method for such studies.

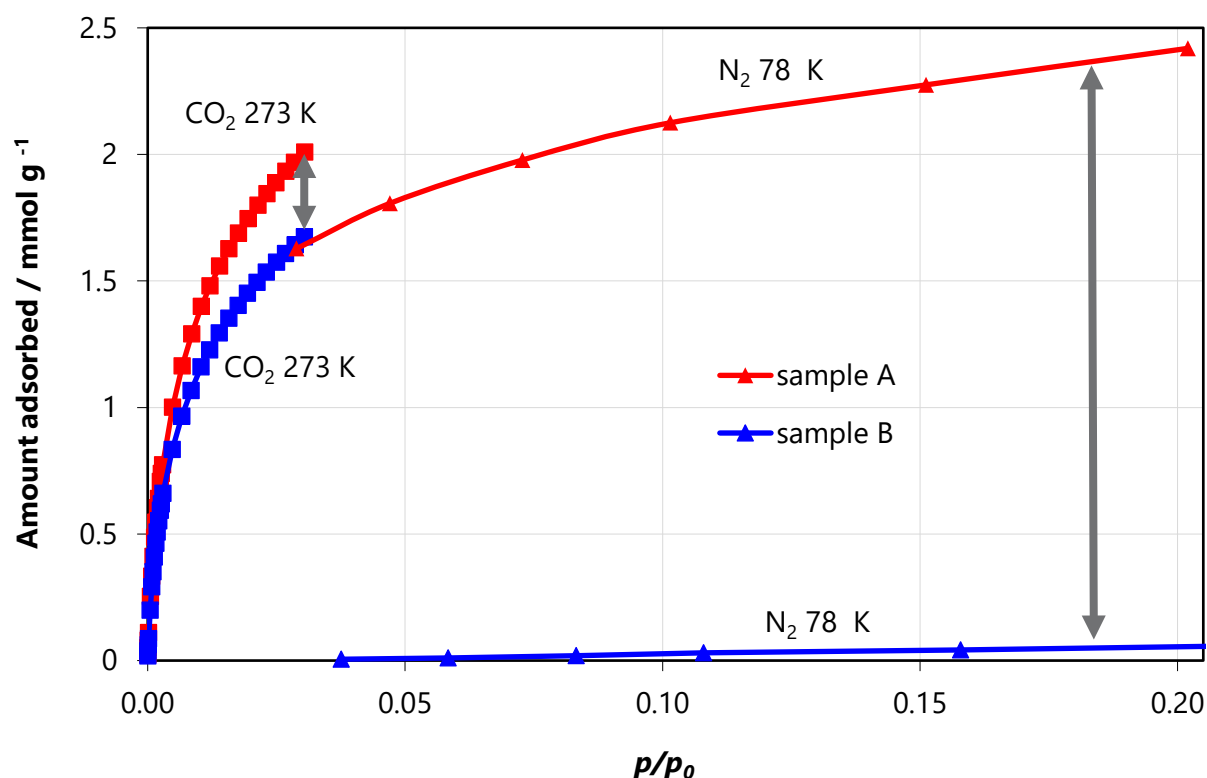


Figure 3 Kinetic hindered N_2 78 K in sample B prevents the investigation of the pore structure with N_2 78 K measurements

How to characterize smallest ultramicropores?

How to characterize ultramicropores < 0.5 nm?

For many materials with micropores, there is no indication before an adsorption measurement if the material contains ultramicropores with pore diameters below 0.5 nm. However, there are few indications during the adsorption isotherm measurement pointing to the effect of hindered adsorption at 78 K:

- a. One has some experience that the material should be microporous, but the N₂ 78 K or Ar 87 K isotherm do not show a Type I isotherm shape.
- b. The BET area value of a probably microporous material is much lower than expected.
- c. The measurement time for the microporous material is much lower in comparison to other microporous materials. That is to explain in the way that N₂ 78 K or Ar 87 K do not diffuse into the smallest material pores (e.g., 0.4 nm and lower) and so the instrument detects a pseudo-equilibration for one data point and continuous with the next one etc.
- d. The measurement time for the microporous material is much higher in comparison to other microporous materials. That is to explain in the way that N₂ 78 K or Ar 87 K diffuse very slowly over long time into the smallest material pores (close to 0.5 nm in that case) and so the instrument detects continuously falling pressure over long time for each data point.

These four observations are indications only for the existence of ultramicropores < 0.5 nm, but no proof. Possible ways for the detection of such pores can be derived from our results shown in Fig. 1 - 3. The N₂ adsorption at 78 K is not a suitable method to detect ultramicropores < 0.5 nm and claims that a classical sorption analyzer can characterize micropores beginning from 0.35 nm by use of the N₂ 78 K method are wrong.

The following ways can be used for the characterization of the complete micropore range:

1. The diffusion rate depends on the size of the adsorbate molecule. As to see from Fig. 1, the smaller H₂-molecule can be used to detect micropores in the range of 0.4 nm.
2. The diffusion rate depends on the temperature. As to see from Fig. 2, a measurement at higher temperature with the same gas can prove the existence of the smallest micropores. Higher volumes adsorbed at higher temperature are an indication for kinetic effects in the smallest micropores.
3. Since the diffusion rate depends on the temperature, another adsorptive at higher temperatures can be a better alternative. Fig. 1 and 3 show CO₂ as alternative with measuring temperatures at 195 K or 273 K, respectively. However, as to see from Fig. 3, CO₂ at 273 K allows only to measure the p/p₀-range below 0.03 with a standard volumetric instrument. Fig. 1 shows the advantage of CO₂ at 195 K with the broader p/p₀-range up to 0.5, which allows more accurate determination of BET area and pore volume. The realization of alternative temperatures with your own sorption analyzer is easily done with a connection of a cryoTune (Fig 4).
4. In addition to the isotherms in Fig. 1, we measured Ar 87 K by use of a cryoTune 87 for Zeolite 4A, too. We found significant higher adsorbed volume in comparison to N₂ 78 K. However, the measurement of this Ar 87 K isotherm took five days and the curve was nevertheless very fidgety because of incomplete equilibration of the measuring points. The conclusion is that Ar has fewer blocking effects on polar groups in ultramicropores because of the measuring temperature (10 K higher) and the absence of a quadrupole moment. This mitigates the problem e.g., for the pore range 0.43 - 0.5 nm, but does not solve it finally for 0.4 nm and below.

How to characterize smallest ultramicropores?

Characterization of
particles • powders • pores

For the Zeolite 4A, we had two indications for kinetic problems, before we changed to CO₂ and H₂ measurements: the unexpected low BET value in combination with no type I shaped isotherm with N₂ 78 K, and the unexpected long isotherm measuring time for a (not equilibrated) fidgety curve with Ar 87 K.



Figure 4 The cryoTune 87 and 195, available for all modern types of sorption analyzers, here in use with the 3P micro 300 sorption analyzer in parallel with different gases at different temperatures.

Conclusion

Ultramicropores smaller as 0.5 nm cannot be measured by standard N₂ isotherms at 78 K, and smaller 0.45 nm also not by Ar 87 K isotherms. Even the best turbo pump, state-of-the-art pressure transducers and the smallest relative pressure points do not help here. Two alternatives are available to detect and study such ultramicropores: increasing the measuring temperature and/or using other adsorptives like CO₂ at 195 K.

For questions and more information, contact us at info@3p-instruments.com or +49-8134 93240.

We are looking forward to your inquiries!

3P Instruments
Rudolf-Diesel-Str. 12
85235 Odelzhausen
Germany
info@3p-instruments.com
+49-8134 93240