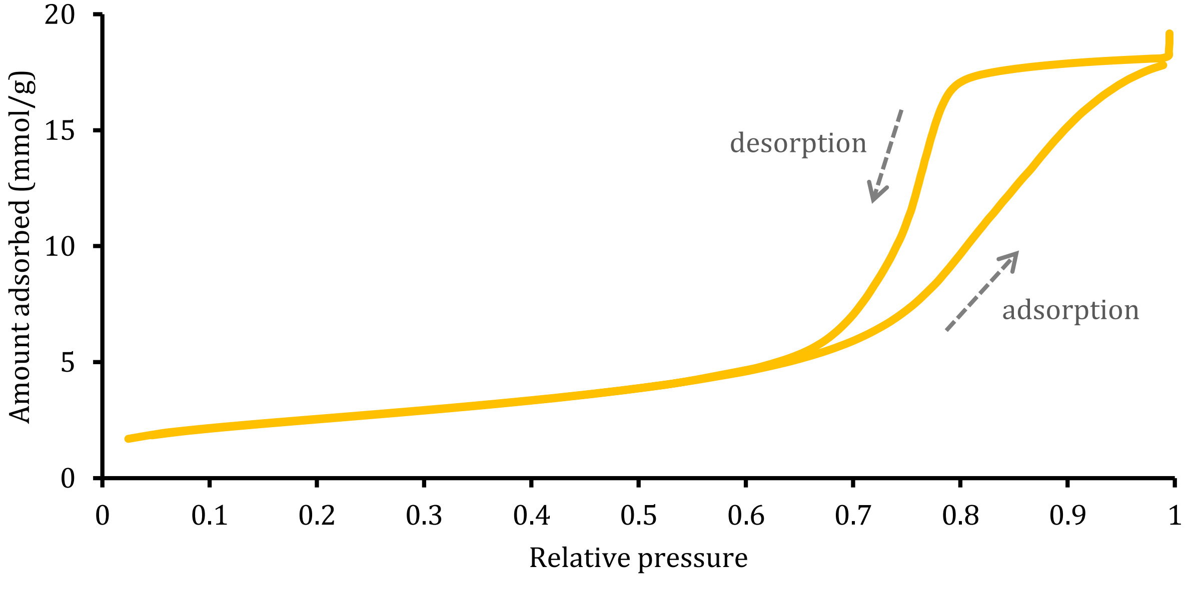
Determining the pore size distribution of mesoporous solids

Introduction

Porous solids have a wide range of applications according to the size and shape of their pores: water purification, hydrogen storage, catalysis of chemical reactions, etc. They are therefore commonly described by their pore size distribution, which relates the amount of pore volume for each pore diameter. In particular, mesopores are defined as pores in the approximate diameter range 2 nm to 50 nm. The pore size distribution is usually derived from a gas adsorption isotherm, experimentally obtained as follows. Successive doses of a gas probe, typically N_2 at 77 K, are sent to the solid material, preliminarily dried and evacuated. The amount of gas molecules that can be adsorbed onto the surface of the solid is derived from the evolution of the pressure in the system. The cumulative amount of gas adsorbed plotted with respect to the pressure is the adsorption isotherm.

Experimental details

- Method: Analysis of mesopores by gas adsorption, ISO 15901-2:2006(E) [1]
- Instrument: *Micromeritics* 3Flex
- Adsorptive gas: N_2 at 77 K
- Sample: reference silica-alumina porous material, dried for 3 h at 350 °C under vacuum (unrestricted from $1.33\cdot10^{-2}$ mbar)
- Amount of sample: 230 mg
- Sample holder: glass tube of 12 mm outer diameter with a seal frit

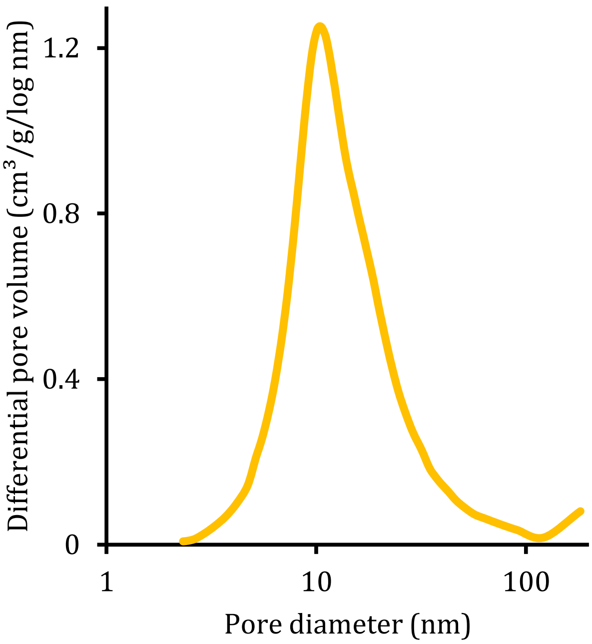


Adsorption isotherm of the reference silica-alumina porous solid. According to the classification of standard physisorption isotherms (IUPAC [2]) this is a type IV isotherm with a hysteresis loop of type H2: it is the signature of a mesoporous solid. The adsorption and desorption branches are different, and a hysteresis loop with non-parallel branches is observed, typical of pores whose size distribution is wide and shape is not well defined.

Results

The adsorption isotherm already contains readable information concerning the size and shape of the pores. But a precise pore size distribution can be derived from it using the Barrett, Joyner and Halenda (BJH) model. This is an algebraic procedure that takes into account the capillary condensate present in the mesopores as well as the multilayer film adsorbed on the walls of the pores. [1]

In the end the pore size distribution on the right is obtained. One peak is visible, which corresponds to the main pore size of the distribution: 12.6 nm in diameter. The area under the peak represents the total pore volume in the solid: 0.65 cm^3/g.



Conclusion

- The distribution of pore size of a mesoporous solid can be extracted from the measurement of its adsorption isotherm using the BJH model.
- The BJH model is only valid for well-defined pore shapes, with minimal interconnection between the pores.
- The quantity needed for that experiment is rather large: at least several hundreds of mg and it needs to be known within 2 % error, as the results are always presented in specific units.
- Pore sizes screened by this method range from 2 nm to 150 nm. For larger pores mercury intrusion may be used.
- This method only works on porous solids that have been dried beforehand, in order to clean the surface and the pores from any adsorbed molecule. This can be done under vacuum or dry gas sweeping, and at high temperature too. If the porous solid cannot undergo drying, thermoporometry may be used: it uses calorimetry instead of volumetry.

[1] *Pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption* — Part 2: Analysis of mesopores and macropores by gas adsorption, ISO 15901-2:2006(E)
[2] Sing K.S.W., Everett D.H., Haul R.A.W., Moscou L., Pierotti R.A., Rouquérol J. and Siemieniewska T., IUPAC Recommendations 1984: Reporting Physisorption Data for Gas Solid Systems with Special Reference to the Determination of Surface Area and Porosity, *Pure & Applied Chemistry* 57, 1985, pp. 603-319