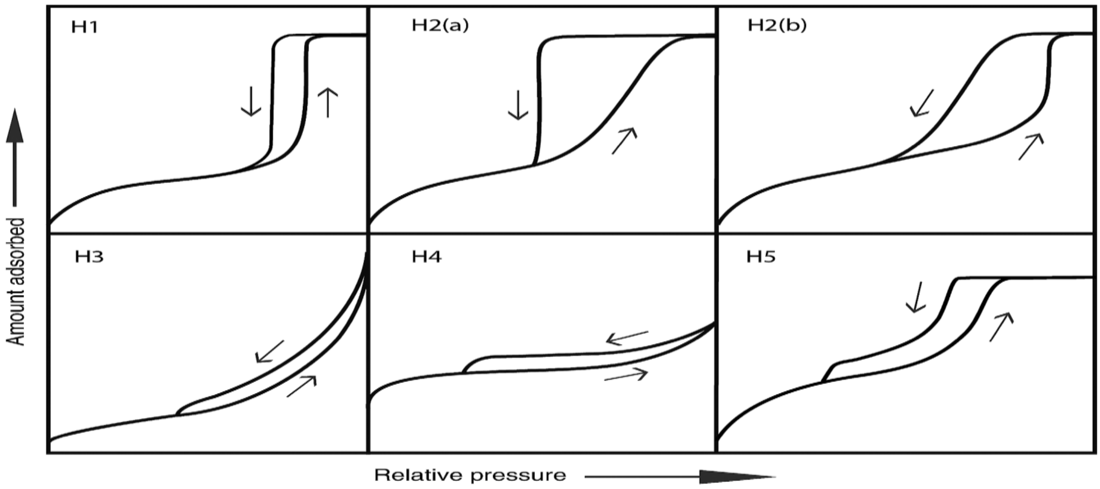
Adsorption hysteresis

Many different shapes of hysteresis loops have been reported, but the main types are shown in Fig.. Types H1, H2(a), H3 and H4 were identified in the original IUPAC classification of 1985, which is in 2015 extended in the light of more recent findings. Each of these six characteristic types is fairly closely related to particular features of the pore structure and underlying adsorption mechanism.



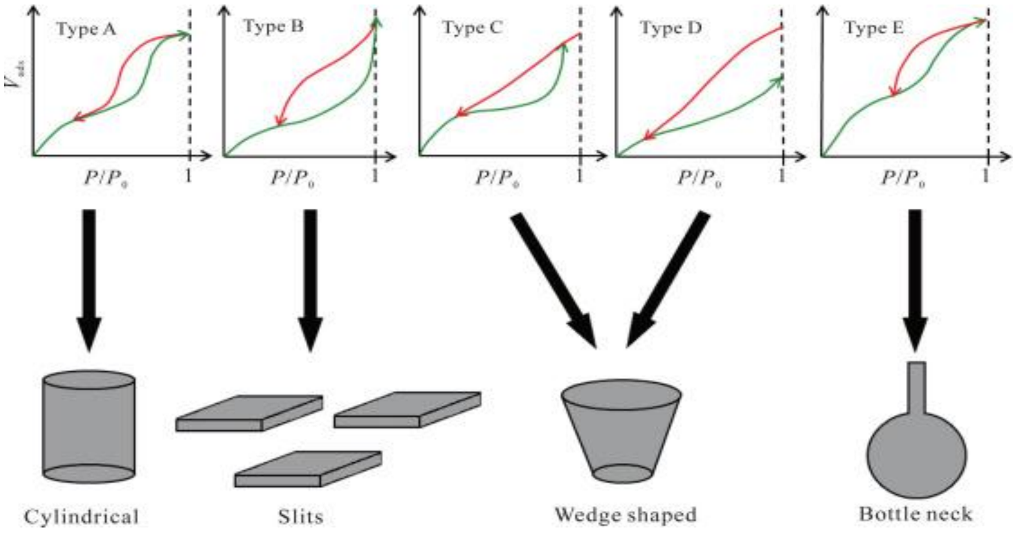
Classification of hysteresis loops

- The Type H1 loop is found in materials which exhibit a narrow range of uniform mesopores, as for instance in templated silicas (e.g., MCM-41, MCM-48, SBA-15), some controlled pore glasses and ordered mesoporous carbons. Usually, network effects are minimal and the steep, narrow loop is a clear sign of delayed condensation on the adsorption branch. However, Type H1 hysteresis has also been found in networks of ink-bottle pores where the width of the neck size distribution is similar to the width of the pore/cavity size distribution.

- Hysteresis loops of Type H2 are given by more complex pore structures in which network effects are important. The very steep desorption branch, which is a characteristic feature of H2(a) loops, can be attributed either to pore-blocking/percolation in a narrow range of pore necks or to cavitation-induced evaporation. H2(a) loops are for instance given by many silica gels, some porous glasses as well as some ordered mesoporous materials (e.g., SBA-16 and KIT-5 silicas).

- The Type H2(b) loop is also associated with pore blocking, but the size distribution of neck widths is now much larger. Examples of this type of hysteresis loops have been observed with mesocellular silica foams and certain mesoporous ordered silicas after hydrothermal treatment.
- There are two distinctive features of the Type H3 loop: (i) the adsorption branch resembles a Type II isotherm, (ii) the lower limit of the desorption branch is normally located at the cavitation-induced $p/p0$. Loops of this type are given by non-rigid aggregates of plate-like particles (e.g., certain clays) but also if the pore network consists of macropores which are not completely filled with pore condensate.
- The H4 loop is somewhat similar, but the adsorption branch is now a composite of Types I and II, the more pronounced uptake at low p/p0 being associated with the filling of micropores. H4 loops are often found with aggregated crystals of zeolites, some mesoporous zeolites, and micro-mesoporous carbons.
- Although the Type H5 loop is unusual, it has a distinctive form associated with certain pore structures containing both open and partially blocked mesopores (e.g., plugged hexagonal templated silicas).

As already indicated, the common feature of H3, H4 and H5 loops is the sharp step-down of the desorption branch. Generally, this is located in a narrow range of $p/p0$ for the particular adsorptive and temperature (e.g., at $p/p0 \sim 0.4 – 0.5$ for nitrogen at temperatures of 77 K).



Assessment of surface area

Principles of the Brunauer–Emmett–Teller (BET) method

The Brunauer–Emmett–Teller method continues to be the most widely used procedure for evaluating the surface area of porous and finely-divided materials, in spite of the weakness of its theoretical foundations.

Indeed, under certain carefully controlled conditions, the *BET-area* of a nonporous, macroporous or a mesoporous solid (i.e., giving a well-defined Type II or a Type IV(a) isotherm) can be regarded as the 'probe accessible area' (i.e., the effective area available for the adsorption of the specified adsorptive).

Two stages are involved in the application of the BET method:

- **First**, it is necessary to transform a physisorption isotherm into the 'BET plot' and from it derive a value of the BET monolayer capacity, $\boldsymbol{n}_{\mathbf{m}}$.

- **In the second stage**, the BET-area, *a*(BET), is calculated from *n*m by adopting an appropriate value of the molecular cross-sectional area, $\boldsymbol{\sigma}_{\mathbf{m}}$.

It is customary to apply the BET equation in the linear form;

$$\frac{p/p^\circ}{\boldsymbol{n}(1-p/p^\circ)}=\frac{1}{\boldsymbol{n}_m C}+\frac{C-1}{\boldsymbol{n}_m C}(p/p^\circ)$$

Where $\boldsymbol{n}$ is the specific amount adsorbed at the relative pressure p/p° and $\boldsymbol{n}_m$ is the specific monolayer capacity.

According to the BET theory, the parameter *C* is exponentially related to the energy of monolayer adsorption. It is now generally agreed that the value of *C* rather gives a useful indication of the shape of the isotherm in the BET range. Thus;

- If the value of *C* is at least ~ 80 the knee of the isotherm is sharp and Point B is fairly well defined (see Fig.). It was this characteristic point which was first identified by Brunauer and Emmett as the stage of monolayer completion and the beginning of multilayer adsorption.

- If C is low (< ~ 50) Point B cannot be identified as a single point on the isotherm. There is then an appreciable overlap of monolayer and multilayer adsorption and the precise interpretation of n_m is questionable. - When C < 2, the isotherm is either Type III or Type V and the BET method is not applicable.

- A high value of C (say, > ~ 150) is generally associated with either adsorption on high-energy surface sites or the filling of narrow micropores.

The derivation of n_m and a_s (BET)

A convenient way to derive $\boldsymbol{n_m}$ from the BET equation is to make use of the linear relation between $(p/p°) / \boldsymbol{n} (1–p/p°)$ and $p/p°$ (i.e., 'the BET plot').

- The range of linearity of the BET plot is always restricted to a limited part of the isotherm, often within the $p/p°$ range of ~ 0.05–0.30 for Type II and Type IVa isotherms. However, in the case of Type IVb isotherms, caution is required since pore condensation may occur at quite low $p/p0$.

- The linear BET range is shifted to lower relative pressures when the adsorption energy is high, especially if the surface is energetically homogeneous or crystalline (e.g., for the adsorption of nitrogen or argon on graphitized carbon or xenon on clean metal films).

- The second stage in the application of the BET method is the calculation of the BET-area from the monolayer capacity. This requires a knowledge of the average area, σ_m *(molecular cross-sectional area)*, occupied by the adsorbate molecule in the complete monolayer. Thus;

$$a_s(\mathrm{BET}) = n_m \cdot L \cdot \sigma_m / m$$

where a_s(BET) is the *BET specific area* of the adsorbent (of mass m).

- Nitrogen (at its boiling temperature, 77 K) was traditionally the adsorptive generally used to obtain a (BET), with $\sigma_m(N_2)$ assumed to be 0.162 nm^2 (based on the assumption of a closed-packed monolayer). This is partly due to the fact that liquid nitrogen was readily available and also because nitrogen isotherms on many adsorbents were found to exhibit a well-defined Point B. However, it is now recognized that due to its quadrupole moment, the orientation of a nitrogen molecule is dependent on the surface chemistry of the adsorbent. This may lead to uncertainty in the value of $\sigma_m(N_2)$ – possibly ~ 20% for some surfaces.

- Argon may seem to be an alternative adsorptive for surface area determination. Argon does not have a quadrupole moment and is less reactive than the diatomic nitrogen molecule. There are, however, several reasons why argon at 77 K is considered to be less reliable than nitrogen. At 77 K, argon is ca. 6.5 K below the bulk triple point temperature and hence the bulk reference state is in doubt. Furthermore, there is evidence that at 77 K, the structure of the argon monolayer is highly dependent on the surface chemistry of the adsorbent (e.g., giving rise to Type VI isotherms on highly uniform surfaces such as graphitized carbons).
- An alternative is argon adsorption at 87 K, i.e., at liquid argon temperature. Here, the problems encountered with argon at 77 K are not present. At 87 K, a cross-sectional area, $\sigma_m(Ar)$, of 0.142 nm^2 is usually assumed.
- Because of the absence of a quadrupole moment and the higher temperature, $\sigma_m(Ar)$ is less sensitive to differences in the structure of the adsorbent surface. Measurements at 87 K can be performed by using either liquid argon (instead of liquid nitrogen) or a cryostat (or cryocooler).
- By using highly accurate manometric adsorption equipment, it is possible to assess surface areas as low as (~ 0.5–1) m^2 with nitrogen or argon as the adsorptive.
- In order to evaluate even lower surface areas, krypton adsorption at 77 K is generally the recommended adsorptive.
- However, the behavior of the krypton at 77 K is in some respect comparable to that of argon at 77 K: at this temperature krypton is well below (by *ca*. 38 K) its triple point and sublimates at *ca*. 0.22 kPa.
- However, evaluation of surface area is complicated by the difficulty in choosing the value of the cross sectional area $\sigma_m(Kr)$, which appears to vary from solid to solid (commonly used values for $\sigma_m(Kr)$ range from ~0.17 to 0.23 nm^2). Since no generally valid recommendations can be made, it is essential to state the chosen

values of $p°$ and σ_m(Kr). In spite of that, krypton adsorption at 77 K is considered to be a very useful tool for routine work on materials with low-surface area.

Porosity analysis

- The pore volume and the pore size distribution can be estimated from gas adsorption, while the hysteresis of the adsorption isotherms can give an idea as to the pore shape.
- In the pores, because of the confined space, a gas will condense to a liquid at pressures below its saturated vapor pressure. The Kelvin equation gives this pressure ratio for cylindrical pores of radius r, where ɣ is the liquid surface tension, V is the molar volume of the liquid, R is the gas constant (about 2 cal mol^{-1} K^{-1}), and T is the temperature. This equation forms the basis of several methods for obtaining pore-size distributions.

$$\ln \frac{p^0}{p} = \frac{2\gamma V}{rRT}$$

The many methods for mesopore size analysis, which make use of the modified Kelvin equation, include those proposed by Barrett, Joyner and Halenda (BJH) and Broeckhoff and de Boer. In order to account for the preadsorbed multilayer film, the Kelvin equation is combined with a standard isotherm (the *t*-curve), which is determined on certain well-defined nonporous solids. However, for the size analysis of narrow mesopores, the standard t-curve is not entirely satisfactory, because the curvature and enhanced surface forces are not properly taken into account. Similarly, the validity of the Kelvin equation is questionable as the mesopore width is reduced because macroscopic concepts can no longer be safely applied.

This was clearly demonstrated with the aid of model mesoporous molecular sieves (e.g., M41S materials). Because of their high degree of order, the pore diameter of such model substances can be derived by independent methods (X-ray-diffraction, high-resolution transmission electron microscopy, etc.). It was shown that the Kelvin equation based procedures, such as the BJH method, significantly underestimate the pore size for narrow mesopores (for pore diameter < ~ 10 nm the pore size will be underestimated by ~ 20–30 %).

Mercury porosimetry

Another method of estimating the pore size distribution of meso- and macropores is by mercury porosimetry. Here one measures the volume of mercury, a non-wetting liquid, which is forced under pressure into the pores of a catalyst sample immersed in mercury. The pressure required to intrude mercury into the sample's pores is inversely proportional to the pore size. For cylindrical pores of radius r, this pressure is given by the Washburn equation, where γ is the surface tension of the liquid, and α is the contact angle. Despite the fact that real pores are rarely cylindrical, this method gives good estimates of pore size distributions.

However, owing to the high contact angle and surface tension of mercury (ca. 140° and $4.8 \times 10^{9} Nm^{-1}$), the measurements are limited to pores wider than 3nm (even these require pressures greater than 4000 bar).

$$r = \frac{2\gamma \cos \alpha}{p}$$

Pressures of 0.1 to 200 MPa allow pore sizes in the range 3.75–7500 nm to be determined. Since the pores are not exactly cylindrical, as assumed in Washburn equation, the calculated pore sizes and pore size distributions can differ considerably from the true values, which can be determined by electron microscopy.

Mercury porosimetry is advantageously used for characterizing various shaped industrial catalysts in which diffusion processes play a role. The macropore distribution is of major importance for the turnover and lifetime of industrial catalysts and is decisively influenced by the production conditions.

Temperature-Programmed Desorption

- Temperature-programmed desorption (TPD) is extensively applied for catalyst characterization. Commonly used molecules are NH_3, H_2, CO and CO_2.
- From the desorption pattern much useful information can be obtained. TPD allows kinetic experiments in which desorption rate from the surface is followed while the

temperature of the substrate is increased continuously in a controlled way, usually in a linear ramp.

- Qualitatively TPD can be interpreted simply because the higher the desorption temperature the more strongly is the adsorbate bonded to the surface.

- Since the area under a TPD curve is proportional to the coverage, TPD spectra allow determination of relative coverages.

TPD is used to determine:

– The adsorbate layer

– The amount of desorbed molecules as a function of the temperature

– The behavior of the catalyst during calcination with an inert carrier gas

– The interaction of probe molecules such as ammonia with zeolites for acidity measurements

- Chemisorbed molecules are bonded to the surface by forces dependent on the nature of the active site. For instance, ammonia will be strongly adsorbed on acid sites, whereas it is only weakly adsorbed on basic sites. Figure 5-45 shows schematically a TPD pattern of ammonia desorption from H-ZSM-5.

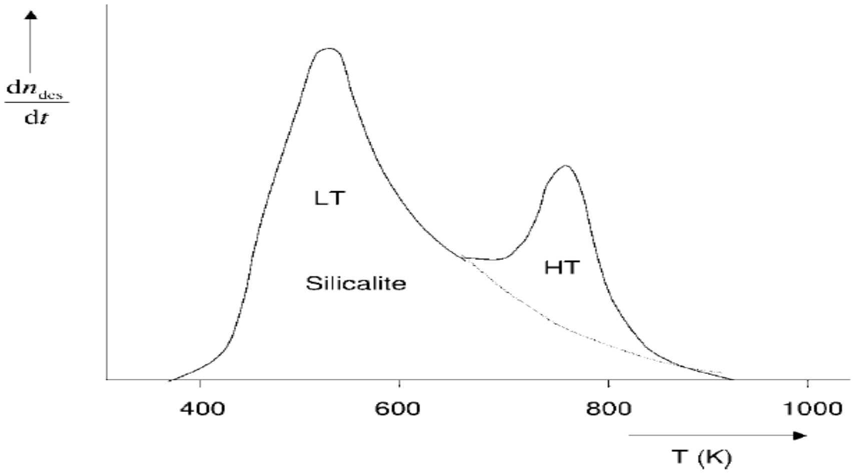


Fig. 5-45 Scheme of a TPD spectrum of ammonia desorbing from zeolite

The desorption spectrum consists of two broad overlapping peaks:

- The first (low temperature LT) peak is assigned to NH_3 desorbing from weak acid or non-acidic sites such as be built from silicalite.

- The high-temperature peak (HT) is due to ammonia desorbed from strong acid sites.

- Thus, the peak temperatures can be correlated to the acid strength of the adsorption sites. But it should be mentioned that the technique does not clearly discriminate between Lewis and Brønsted sites.

Chemical Characterization and Surface Analysis

Of particular importance is the composition, i. e., the distribution of elements in the catalyst, and the detection of phases and surface compounds. Also of interest are differences in composition between catalyst volume and catalyst surface, as well as interactions between active components and support materials and between the active components themselves.

These phenomena are best studied by advanced spectroscopic methods. Since the solid surface plays the decisive role in heterogeneous catalysis, methods for the characterization of surfaces are of major importance in modern catalyst research.

Catalyst surfaces, surface compounds, metals dispersed on supports, and adsorbed molecules are investigated by electron spectroscopy, ion spectroscopy, analytical microscopy, and other methods.

We will first discuss methods with which the structure of the surface is determined, and then those that determine the chemical composition of the surface (catalyst and substrate). Finding relationships between the structures of material and the catalyst activity requires high-resolution investigation of the microstructure of the catalyst. Since heterogeneous catalysts are often highly nonuniform solids, correct sampling, sample preparation, and choice of the appropriate method are important if meaningful results are to be obtained.