Characterization of porous solids and powders: Density, surface area and pore size

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0. Motivation
1. Introduction
2. Gas adsorption
3. Density measurements
4. Adsorption isotherms
5. Surface area determination
6. Mesopore analysis

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Catalysis: Nanostructured materials as support

- High(er) specific surface area of nanostructured materials
  - increased activity
  - formation of isolated, catalytic sites

...an estimate based on a material with spherical particles using

\[ S = \frac{4 \pi r^2}{m} \]

\[ m = \frac{4}{3} \rho \pi r^3 \]

with \( \rho \sim 3 \text{ g/cm}^3 \) (typ. oxide value)

shows that for

- \( r = 1 \text{ cm} \) \( \Rightarrow S = 10^{-2} \text{ m}^2/\text{g} \)
- \( r = 1 \mu\text{m} \) \( \Rightarrow S = 1 \text{ m}^2/\text{g} \)
- \( r = 1 \text{ nm} \) \( \Rightarrow S = 1000 \text{ m}^2/\text{g} \)

\( \Rightarrow \) Creation of high surface requires nanoscale structuring
Novel mesoporous silica molecular sieve: SBA-15

TEM characterization

along a longitudinal section in a section of hexagonal pores

⇒ Silica SBA-15 is a very ordered large-pore (7 nm) material
Model catalysts based on mesoporous SBA-15

- Support properties are well defined (structural homogeneity) and tunable (pore diameter)
  - control over support properties
  - well-structured silica platform for vanadia catalysts

⇒ 3-D model catalyst for partial oxidation reactions

$\text{VO}_x$/SBA-15
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Real surfaces - Factors affecting surface area

• Idealization: cube → $S = 6 \ l^2$
  sphere → $S = 4 \ \pi \ r^2$

  *Reality*: Surface roughness due to voids, pores, steps, other imperfections and surface atomic and molecular orbitals

  → real surface area > corresponding theoretical area

• **Particle size**: e.g. cube $l = 1 \ \text{m} \rightarrow S = 6 \ \text{m}^2$
  $l = 1 \ \mu\text{m} \rightarrow S = 6 \ 10^{-12} \ \text{m}^2$
  $N = 10^{18} \rightarrow S = 6 \ 10^6 \ \text{m}^2$

• **Particle shape**: e.g. two particles with same composition and mass

  \[ M_{\text{cube}} = M_{\text{sphere}} \]
  \[ (V\delta)_{\text{cube}} = (V\delta)_{\text{sphere}} \]
  \[ l^3_{\text{cube}} = \frac{4}{3} \ \pi \ r^3_{\text{sphere}} \]
  \[ (S_{\text{cube}} \ l_{\text{cube}})/6 = S_{\text{sphere}} \ r_{\text{sphere}}/3 \]

  \[
  \frac{S_{\text{cube}}}{S_{\text{sphere}}} = 2 \ \frac{r_{\text{sphere}}}{l_{\text{cube}}}
  \]
Factors affecting surface area

• **Porosity**: can overwhelm size and shape factors
e.g. powder consisting of spherical particles

\[
S_t = 4 \pi (r_1^2 N_1 + r_2^2 N_2 + \ldots + r_i^2 N_i) = 4 \pi \sum r_i^2 N_i
\]

\[
V = 4/3 \pi (r_1^3 N_1 + r_2^3 N_2 + \ldots + r_i^3 N_i) = 4/3 \pi \sum r_i^3 N_i
\]

\[
S = S_t/M = 3 \sum r_i^2 N_i/\delta \sum r_i^3 N_i
\]

for spheres of uniform radius: \[ S = 3/\delta \ r \]

with \( r \sim 3 \text{ g/cm}^3 \) (typ. oxide value):

\[ r = 1 \text{ cm} \rightarrow S = 10^{-2} \text{ m}^2/\text{g} \]

\[ r = 1 \text{ mm} \rightarrow S = 1 \text{ m}^2/\text{g} \]

\[ r = 1 \text{ nm} \rightarrow S = 1000 \text{ m}^2/\text{g} \]
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Introduction

• most popular method for surface and pore size characterization (0.35-100nm)
  other methods include: - small angle X-ray scattering (SAXS)
    - neutron scattering (SANS)
    - electron microscopy (scanning and transmission)
    - NMR methods
    - mercury porosimetry

• adsorption: enrichment of components in interfacial layer
  gas adsorption → gas/solid interface

  \[ W = f(P,T,E) \]

  \( W \): weight of gas adsorbed (per unit weight adsorbent)
  \( E \): interaction potential between adsorbate and adsorbent

  \( T = \text{const.} \) → \( W = f(P,E) \)

  plot of \( W \) vs. \( P \) referred to as sorption isotherm
Physical adsorption forces

- Physical adsorption forces
  Thermodynamics: \( \Delta G = \Delta H - T\Delta S \)
  \( \rightarrow \Delta H \) always negative for adsorption

- van der Waals’ forces: *dispersion forces*, ion-dipole, ion-induced dipole, dipole-dipole, quadrupole

- *physisorption* on a planar surface:
  London-van der Waals’ interaction energy:
  \[
  U_s(z) = C_1 z^{-9} - C_2 z^{-3}
  \]
  \( C_1, C_2 \): constants

  \( \rightarrow \) surface excess: \( n^\sigma = n^g - \delta^g V^g \)

  \[
  n^g = n_{ads} + n_{bulk} \]
  \[
  V^g = V_{ads} + V_{bulk} \]

  \[
  n^\sigma = n_{ads} - \delta^g V_{ads} = (\delta_{ads} - \delta^g)V_{ads}
  \]

  \( \rightarrow \) at low \( T \): \( \delta^g << \delta_{ads} \Rightarrow n^\sigma \sim n_{ads} \)

  (e.g. \( \text{N}_2 \) adsorption at 77K)
Experimental

- Experimental
  measure $n_{ads}$ vs P under static or quasi-equilibrium conditions using
  - *volumetric* (manometric) methods
  - *gravimetric* methods

**Gravimetric method:**
based on sensitive microbalance and pressure gauge
→ adsorbed amount measured directly (sensitivity $\sim 10^{-8}$ g)
→ adsorbent not in direct contact with thermostat (→ T control difficult!)

**Volumetric method:**
based on calibrated volumes
and pressure measurements
→ known amounts of gas are admitted stepwise into cell
→ $V_{ads}$ difference between gas admitted and gas filling void volume
→ requires manifold ($V_m$) and void volume ($V_v$) to be accurately known
Experimental

→ $V_m$ determination via expansion of He into calibrated reference volume $V_R$

\[
\frac{P_1 V_m}{T_m} = \frac{P_2 (V_m + V_R)}{T_m}
\]

→ $V_v$ determination via expansion of He into sample cell volume occupied by adsorbent

\[
\frac{P_3 V_m}{T_m} = \frac{P_4 (V_m + V_v)}{T_m}
\]

→ total volume of adsorptive dosed: $V_d = \left( \frac{P_m V_m}{T_m} - \frac{PV_m}{T_{mc}} \right) \times \frac{T}{P}$

→ adsorbed volume: $V_s = V_d - V_v$

→ correction for non-ideality of real gases: $V_s = V_d - (V_v + PV_v \alpha)$

$\alpha$: non-ideality factor

e.g. $N_2$: $\alpha = 6.6 \times 10^{-5}$ torr$^{-1}$(77K)
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• Density measurements
e.g. for permeametry
volume specific surface area

true density = \frac{\text{mass}}{\text{volume occupied by mass}}

→ contribution by pores/internal voids must be subtracted

No porosity: true density measured by displacement of fluid
→ accuracy: fluid volume determination

Porosity: fluid displaced by powder does not penetrate (all) pores
→ apparent density < true density
→ true density via gas displacement (pycnometer)
using e.g. He (inert, small size)
Experimental

• sample cell:

\[ P_a (V_c - V_p) = n_a R T_a \quad (1) \]
\[ P_1 (V_c - V_p) = n_1 R T_a \quad (2) \]

• open valve 2:

\[ P_2 (V_c - V_p + V_R) = n_1 R T_a + n_R R T_a \]
\[ P_a V_R \]

(2) in (3): \[ P_2 (V_c - V_p + V_R) = P_1 (V_c - V_p) + P_a V_R \quad (4) \]

\[ V_p = V_c + V_R \frac{1 - (P_a / P_2)}{1 - (P_1 / P_2)} \]
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Pore size and adsorption potential

- **Classification:**
  - Macropore: $d > 50\text{nm}$
  - Mesopore: $2\text{nm} < d < 50\text{nm}$
  - Micropore: $d < 2\text{nm}$

- **Internal Pore Width:**
  - Nearly flat surface
  - Fluid-wall and fluid-fluid i.a.
    - (→ capillary condensation)
  - Fluid-wall i.a., overlapping ads. potential
Classification of adsorption isotherms

- **classification** → IUPAC 1985

- **type I**: ads. limited to a few layers (chemisorption, micropores)

- **type II**: unrestricted mono/multilayer ads. → at point B monolayer (non-porous, macropores)

- **type III**: unrestricted multilayer ads.

- **type IV**: monolayer/multilayer ads., limited uptake, hysterisis due to pore condens. (mesopores)

- **type V**: multilayer ads. (→ type III), pore condensation (hysterisis)

- **type VI**: stepwise multilayer ads. on a uniform, non-porous surface
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Langmuir isotherm

- Langmuir isotherm: → applicable to chemisorption and type I physisorption
  - identical adsorption sites
  - no interactions between adsorbed molecules
  - \(\Delta H_{\text{ads}} \neq f(\theta)\)

adsorption of A: \(v_a = k_a P (1 - \theta)\)
desorption of A: \(v_a = k_a \theta\)
equilibrium: \(k_a P (1 - \theta) = k_a \theta\)

\[
\theta = \frac{KP}{1 + KP} \quad K = \frac{k_a}{k_a}
\]

\[
\theta = \frac{V}{V_m}
\]

substitute/rearrange:

\[
\frac{1}{V} = \frac{1}{V_m} + \frac{1}{V_m KP}
\]

plot \(1/V\) vs \(1/P\) → straight line:
intercept \(1/V_m\) → \(n_{\text{ads}}\)

surface area: \(S_t = n_{\text{ads}} N_A A_x\)  \(A_x\): cross-sectional area
Brunauer, Emmett and Teller (BET) theory

- BET isotherm:
  - first layer serves as substrate for further adsorption (physisorption)
  - almost universally used → accommodates isotherm types I-V

→ derivation BET

BET isotherm: \[
\frac{1}{V[(P_0 / P) - 1]} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \left( \frac{P}{P_0} \right)
\]

C: BET constant

\( V_m \rightarrow n_{ads} \)

surface area: \[
S_t = n_{ads} N_A A_x
\]

\( n_{ads} M = W \)
Single point BET method

\[
\frac{1}{W[(P_0/P) - 1]} = \frac{1}{W_mC} + \frac{C - 1}{W_mC} \left(\frac{P}{P_0}\right)
\]

plot \(1/W[(P_0/P)-1]\) vs \(P/P_0\)

→ usually straight line

within \(0.05 < P/P_0 < 0.35\)

intercept: \(b = \frac{1}{W_mC}\)

slope: \(m = \frac{C - 1}{W_mC}\)

\[W_m = \frac{1}{b + m}, \quad C = \frac{m}{b} + 1\]

• Single point BET method: → simplicity and speed with little loss of accuracy

\[\frac{m}{b} = C - 1\]

for large values of \(C\) → \(m \gg b\)

→ \(b \approx 0\)

\[\frac{1}{W[(P_0/P) - 1]} = \frac{C - 1}{W_mC} \left(\frac{P}{P_0}\right)\]
Comparison of single point and multipoint methods

\[
\frac{(W_m)_{mp} - (W_m)_{sp}}{(W_m)_{mp}} = \frac{1 - P / P_0}{1 + (C - 1)P / P_0}
\]

mp: multipoint
sp: single point

<table>
<thead>
<tr>
<th>C</th>
<th>(P/P_0 = 0.1)</th>
<th>(P/P_0 = 0.2)</th>
<th>(P/P_0 = 0.3)</th>
<th>((P/P_0)_m^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.90</td>
<td>0.80</td>
<td>0.70</td>
<td>0.50</td>
</tr>
<tr>
<td>10</td>
<td>0.47</td>
<td>0.29</td>
<td>0.17</td>
<td>0.24</td>
</tr>
<tr>
<td>50</td>
<td>0.17</td>
<td>0.07</td>
<td>0.04</td>
<td>0.12</td>
</tr>
<tr>
<td>100</td>
<td>0.08</td>
<td>0.04</td>
<td>0.02</td>
<td>0.09</td>
</tr>
<tr>
<td>1000</td>
<td>0.009</td>
<td>0.004</td>
<td>0.002</td>
<td>0.003</td>
</tr>
</tbody>
</table>

*(P/P_0)_m^* is the relative pressure that gives monolayer coverage according to a multipoint determination.

BET isotherm: \(W = W_m\)

\[
\rightarrow \left( \frac{P}{P_0} \right)_m = \frac{\sqrt{C - 1}}{C - 1}
\]

\[
\rightarrow \frac{(W_m)_{mp} - (W_m)_{sp}}{(W_m)_{mp}} = \frac{\sqrt{C - 1}}{C - 1} = \left( \frac{P}{P_0} \right)_m
\]
Applicability of the BET theory

- accommodates isotherm types I-V
- good agreement between theory and exp. within $0.05 < P/P_0 < 0.30$

why?

- variation from linearity at $P/P_0 > 0.30$
  $\rightarrow \Delta H_{\text{ads}}$ varies throughout the layers
- porosity: micropores/mesopores $\sim$2-4nm
  pore filling $\leftrightarrow$ mono/multilayer
Cross-sectional area

Surface area: \( S_t = n_{ads} N_a A_x \)  
\( A_x \): cross-sectional area (temperature, ads.-ads. i.a., ads.-surface i.a., texture)

- Approximation of \( A_x \) of adsorbate molecules
  → spherical, exhibiting bulk liquid properties

\[
A_x = 1.091 \times \left( \frac{\bar{V}}{N_A} \right)^{2/3}
\]

<table>
<thead>
<tr>
<th>Adsorptive Temperature</th>
<th>Cross-sectional area (Å²)[15]</th>
<th>Customary Value (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen 77.35 K</td>
<td>13.0 - 20.0</td>
<td>16.2</td>
</tr>
<tr>
<td>Argon 77.35 K</td>
<td>10.0 - 19.0</td>
<td>13.8</td>
</tr>
<tr>
<td>Argon 87.27 K</td>
<td>9.7 - 18.5</td>
<td>14.2</td>
</tr>
<tr>
<td>Krypton 77.35 K</td>
<td>17.6 - 22.8</td>
<td>20.2</td>
</tr>
<tr>
<td>Xenon 77.35 K</td>
<td>6.5 - 29.9</td>
<td>16.8</td>
</tr>
<tr>
<td>Carbon Dioxide 195 K</td>
<td>14 - 22.0</td>
<td>19.5</td>
</tr>
<tr>
<td>Carbon Dioxide 273 K</td>
<td></td>
<td>21.0</td>
</tr>
<tr>
<td>Oxygen 77.35 K</td>
<td>13 - 20</td>
<td>14.1</td>
</tr>
<tr>
<td>Water 298.15 K</td>
<td>6 - 19</td>
<td>12.5</td>
</tr>
<tr>
<td>n-Butane 273.15 K</td>
<td>36 - 54</td>
<td>44.4</td>
</tr>
<tr>
<td>Benzene 293.15 K</td>
<td>73 - 49</td>
<td>43.0</td>
</tr>
</tbody>
</table>

→ \( N_2 \) is standard BET adsorptive

- Surfaces of high polarity (such as silica) may show significant deviation…
e.g. \( N_2 \) (77.35 K): \( A_x = 13.5 \) Å²
known amount of air is drawn through compacted bed of powder → resistance to air flow is a function of the surface area

- ambient $p$ and $T$ ($\lambda < d$): gas collisions → viscous flow → ignores blind pores → `envelope` area of particle
- reduced $p$ ($\lambda \approx d$): → no flow retardation near wall
- small $p$ ($\lambda > d$): gas-wall collisions (→ diffusion) → senses blind pores and gives good agreement with BET

viscous flow through cylindrical pores → Poiseuille

$$S^2 = \left( \frac{\Delta P}{l} \right) \left[ \frac{p^3}{(1 - p)^2} \right] \left( \frac{1}{f\delta^2\eta v} \right)$$

$p$: porosity, $v$: velocity

$$f = 2\left(\frac{l}{l_p}\right)^2$$

aspect ratio

→ aspect ratio highly dependent upon particle size and shape (typically $f = 3-6$)
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Adsorption in mesopores - multilayer adsorption

- Adsorption in mesopores:
  depends on fluid-wall and attractive fluid-fluid interactions
  → multilayer adsorption and pore condensation
  - novel ordered mesoporous materials (e.g. MCM, SBA)
  - Microscopic methods (e.g. NLDFT)

- Multilayer adsorption:
  Fluid in contact with planar surface
  → thickness \( l \): \( l \rightarrow \infty \) for \( P/P_0 \rightarrow 1 \)

\[
\Delta \mu_a = \mu_a - \mu_0 = -RT \ln(P/P_0) \\
= -\alpha \times l^{-m} \\
\text{(m typ. 2.5-2.7)}
\]

\( \alpha \): fluid-wall interaction parameter
\( \mu_a \): chem. potential of adsorbed liquid-like film
\( \mu_0 \): chem. potential of bulk fluid at gas-liquid coexistence
Pore condensation – modified Kelvin equation

• in pore l can not grow unlimited

\[ \Delta \mu = \Delta \mu_a + \Delta \mu_c \]

for small l: \[ \Delta \mu \approx \Delta \mu_a = -\alpha \times l^{-m} \]

for large l: \[ \Delta \mu \approx \Delta \mu_c = -2 \gamma \cos \theta / a \Delta \rho \]

a: core radius
(a = r_p - l; r_p: pore radius)

\( \gamma \): surface tension
\( \Delta \rho = \rho^l - \rho^g \)

• at critical thickness \( l_c \):

_***pore condensation*** (i.e. gas-like state → liquid-like state at \( \mu < \mu_0 \))

**Kelvin equation:**

\[ \ln(P / P_0) = \frac{-2 \gamma \bar{V}}{aRT} \]

for complete wetting, i.e. \( \theta = 0 \)
Methodes based on modified Kelvin equation

- Calculation of the pore size distribution:
  - from isotherm: $V_{ads}/g$ catalyst as function of $P/P_0$
  - Kelvin equ.: calculate $a$ for $\theta=0$ as function of $P/P_0$
  - calculate statistical film thickness $I$: $l = (W_a/W_m)\tau \rightarrow r_p = a - l$
  - calculate $\bar{a}$ and $\bar{r}_p$ in each decrement from successive entries
  - calculate $\Delta I$, the change in film thickness in successive steps
  - calculate $\Delta V_{ads}$, the change ads. volume in successive steps
  - calculate $\Delta V_{liq}$, corresponding to $\Delta V_{ads}$
  - calculate $\Delta l \Sigma S$, the volume change of film remaining adsorbed
  - calculate the pore volume $V_p$:
    $$\begin{align*}
    \Delta V_{liq} &= \pi \cdot \bar{a} \cdot l_p + \Delta l \Sigma S \\
    V_p &= \pi \cdot \bar{r}_p^2 \cdot l_p \\
    V_p &= \left(\frac{\bar{r}_p}{\bar{a}}\right)^2 [\Delta V_{liq} - (\Delta l \Sigma S)]
    \end{align*}$$
  - calculate the surface area $S$: $S = \frac{2V_p}{\bar{r}_p}$
Testing the modified Kelvin equation

• direct exp. test of Kelvin eq. (MCM, SBA) and comparison with XRD, TEM results → Kelvin eq. underestimates pore size

• accurate pore size analysis by applying microscopic models based on stat. mech. → local fluid structure near curved wall → capture properties of confined fluid
**Adsorption vs desorption branch of hysteretic isotherm**

- ordered mesoporous materials
  → desorption branch of hysteresis loop reflects equilibrium phase transition
- disordered mesoporous materials
  → desorption branch not necessarily correlated with the pore size
  e.g. tensile strength effect → artifact!
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