Structural Characterization
of
Nano-porous Materials

奈米孔洞材料的結構鑑定
Techniques for characterization of nano-porous materials

Crystalline structure
- Single crystal & Powder X-ray diffraction (XRD)
- Electron crystallography

Oxidation state & Coordination
- X-ray absorption spectra
- X-ray photoelectron spectra (XPS & Auger)
- Solid state NMR (mainly coordination)
- IR & Raman (mainly coordination)
- UV-Vis spectra

Elemental analysis- ICP-AES, XPS, EDX

Surface area & Pore size
- N₂ adsorption-desorption isotherm
- Mercury Intrusion Porosimetry

Morphology- SEM
Pore structure- TEM
Structural Determination

- Long distance ordered-arrangement of atoms
  - Single crystal & Powder X-ray diffraction (XRD)
    Electron crystallography

- Long distance ordered-arrangement of pores
  - XRD, Electron crystallography

- Local arrangement of atoms (coordination environment)
  - X-ray absorption spectra (XAS)
  - Solid state NMR
  - IR & Raman

- Oxidation state
  - X-ray photoelectron spectra (XPS), XAS
  - UV-Vis spectra
The Electromagnetic Spectrum

Approximate frequencies, Hz

\[10^{24} \quad 10^{22} \quad 10^{20} \quad 10^{18} \quad 10^{16} \quad 10^{14} \quad 10^{12} \quad 10^{10} \quad 10^8 \quad 10^6 \quad 10^4 \quad 10^2 \quad 10^0\]

γ rays

X rays

Cellular phones

AM Radio

60 Hz (AC current)

Radio

Microwave

FM Radio

Extra low frequency (ELF)

Approximate wavelengths, m

\[10^{-16} \quad 10^{-14} \quad 10^{-12} \quad 10^{-10} \quad 10^{-8} \quad 10^{-6} \quad 10^{-4} \quad 10^{-2} \quad 10^0 \quad 10^2 \quad 10^4\]

Visible

\[\lambda = 390 \quad 450 \quad 500 \quad 550 \quad 600 \quad 650 \quad 700 \quad 760 \text{ nm}\]
Figure 12-4 Partial energy-level diagram showing common transitions producing X-rays. The most intense lines are indicated by the wider arrows.
In 1912 Max von Laue reported the diffraction of X rays by a crystal (for which he received a Nobel Prize in physics in 1914). The elder Bragg and his son, who was by then a doctoral student with J. J. Thomson at Cambridge, began exploring this phenomenon immediately. They brought different interests and skills to the collaboration. William Henry’s original interest was in what diffraction showed about the nature of X rays, and he was a skilled experimenter and designer of instruments. William Lawrence was more concerned with what X rays revealed about the crystalline state, and he possessed a powerful ability to conceptualize physical problems and express them mathematically. Simple inorganic crystals like sodium chloride were the subjects of the original studies in X-ray crystallography. Here the surprising result was that in the solid state these ionic compounds did not exist as paired positive and negative ions. Sodium chloride, for instance, did not exist as NaCl units; rather, Na and Cl alternated in a regular fashion in the crystal lattice.

In 1915, Bragg received the Nobel Prize.
X-Ray Diffraction Image & Pattern

Single crystal

Powder
Mordenite

Idealized cell constants: orthorhombic, Cmcm, a = 18.3 Å, b = 20.5 Å, c = 7.5 Å

See Appendix A for 8-ring viewed along [010]
As-synthesized

(calcined)

Fig. 4 The channel structure in ZSM-5.
Discovery of M41S Family

SBA-15

Cubic Hexagonal

Structures and Low-Angle XRD patterns of Nano-porous Silica

In-situ phase transformation studies

Ming-Chang Liu, and Soofin Cheng

*Department of Chemistry, National Taiwan University
Figure 2. Changes in powder X-ray diffraction patterns during synthesis of the carbon molecular sieve CMK-1 with its silica template MCM-48: (a) The mesoporous silica molecular sieve MCM-48, (b) MCM-48 after completing carbonization within pores, and (c) CMK-1 obtained by removing silica wall after carbonization. These XRD patterns were obtained using a Rigaku D/MAX-III (3 kW).
Fig. 2. XRD pattern and TEM image of CMK-1 carbon after the complete removal of template.

**MCM-48**

Fig. 3. XRD pattern and TEM image of CMK-2 carbon after the complete removal of template.

**SBA-1**

Fig. 4. XRD pattern and TEM image of CMK-3 carbon after the complete removal of template.

**SBA-15**
Overlapping of peaks?

Difficulties in solving the crystal structure from X-ray powder diffraction patterns
Structural Determination

• Long distance ordered-arrangement of atoms
  - Single crystal & Powder X-ray diffraction (XRD), Electron crystallography

• Long distance ordered-arrangement of pores
  - XRD, Electron crystallography

• Local arrangement of atoms (coordination environment)
  - X-ray absorption spectra
  - Solid state NMR
  - IR & Raman

• Oxidation state
  - X-ray photoelectron spectra (XPS)
  - UV-Vis spectra
Two HRTEM (high-resolution TEM) images. The left image reveals a buried hexagonal phase in cubic CdTe. The right image shows the atomic structure of planar defects in thin-film silicon: a twin defect (in which the upper layers are rotated 180° from the lower layers), an intrinsic stacking fault (ISF—in which adjacent layers are shifted slightly), and an extrinsic stacking fault (ESF—in which there is an intervening layer between two layers slightly shifted from each other).
Figure 3.46 High-resolution micrographs (middle) together with selected-area diffraction patterns and optical micrographs of ZSM-5 looking down the [010] direction (top left) and the [100] direction (top right). Corresponding views of the structural model are shown at the bottom. (Based on work of G.R. Millward and J.M. Thomas).
de Broglie relation
\[ \lambda = \frac{h}{mv} \]

Electron diffraction crystallography
Structural Solution of Mesocaged Material AMS-8

Alfonso E. Garcia-Bennett,* Kelichi Miyasaka, and Osamu Terasaki


Figure 1. X-ray diffraction pattern of calcined AMS-8 cubic mesocaged structure with unit cell parameter $a = 183.4$ Å.

Figure 2. Nitrogen adsorption–desorption isotherm of calcined AMS-8. The isotherm shows a relatively broad capillary condensation step accompanied by a marked hysteresis effect in desorption branch of the isotherm.

Figure 3. Typical HRTEM images and corresponding FT diffractograms of calcined AMS-8 recorded with (a) [100], (b) [110], (c) [111], and (d) [211] incidence. Diffractograms are indexed on the basis of a cubic unit cell, $a = 177.9$ Å. All images show large ordered regions indicative of a well-structured material.
Figure 4. Plot of pore volume fraction versus potential density of the wall for mesocaged material AMS-8 (a), from which the 2D-sliced electrostatic potential density maps of the unit cell can be derived for the threshold range 150–256 (b) and the threshold values 189 (c) and 199 (d). The latter correspond to 44 and 50% pore volume fractions, respectively. The unit cells slices are taken with $z = 7$, where the unit cell has been divided into 100 slices (slice thickness = 1.834 Å). White contrast represents the silica wall and black contrast represents the pore space.
Figure 5. Electron density 3D reconstruction of the unit cell of AMS-8 viewed in perspective along the [100] (top), [110] (middle), and [111] (bottom) directions for threshold values 189 (left) and 199 (right). Only the outline of the cages is shown where light red corresponds to the interior surface of the cage. For threshold 189, large cages are connected via cavity windows to four additional large cages in a zigzag arrangement. This connecting window can be clearly seen as a pore opening parallel to the [110] orientation. Smaller cages are not connected. For threshold 199, large cages are connected to 12 individual smaller cages through small openings and to 4 additional larger cages through larger openings. Smaller cages are connected to each other through a single small pore opening.
Particle Size Determination from XRD peaks

- The width of the peaks in a powder pattern contain information about the crystallite size in the sample (and also the presence of microstrain)
- $L = \frac{K \lambda}{\beta \cos \theta}$: Scherrer equation
  - $L$ - mean size of crystallites
  - $K$ - constant roughly 1: depends on shape of crystallites
  - $\beta$ - width of reflection in radians
**XRD Pattern of Meso-Porous ZrO$_2$**

![XRD Pattern](image)

**Scherrer Equation**

$$d = \frac{K \lambda}{\beta^{1/2} (\cos \theta)}$$

$$\beta^{1/2} = \sqrt{(B^2 - b^2)}$$

(calibrated peak width at half maximum)

$B = \text{peak width at half maximum}$

$b = \text{instrumental peak width}$

($\sim 0.16$ for NaCl$_{(s)}$)
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**Morphology** - SEM

**Pore structure** - TEM
Survey on Pore Size Determination Methods
$\text{N}_2$ or Ar Adsorption-Desorption Isotherm

Figure 3.1. The six basic adsorption isotherm types.
Figure 3.2. Adsorption and desorption isotherms for a nonporous solid.

Figure 3.6. Adsorption and desorption isotherms for a microporous solid. The inset shows the steep rising region of the isotherm plotted on a logarithmic x-axis.
b. $N_2$ adsorption -

Non-porous

**Figure 3.2.** Adsorption and desorption isotherms for a nonporous solid.

Capillary condensation applicable to **mesopore only**

$20 \text{ Å} < d < 500 \text{ Å}$

**Figure 3.3.** Adsorption and desorption isotherms for a porous solid.
Explanation for hysteresis

(1) Changes in Contact Angles upon Ads. & Des.

On adsorption,
According to Kelvin eq.

\[
\ln \frac{P_a}{P_0} = - \frac{2 s \bar{V} \cos \theta}{RT r_k} \quad \frac{P_a}{P_0} = e^{-\frac{2 s \bar{V} \cos \theta}{RT r_k}}
\]

radius of empty pore

molar volume of liquid

surface tension of liquid

On desorption, \( \theta = 0 \), \( \cos \theta = 1 \)

\[
\ln \frac{P_d}{P_0} = - \frac{2 s \bar{V}}{RT r_k} \quad \frac{P_d}{P_0} = e^{-\frac{2 s \bar{V}}{RT r_k}}
\]

Since \( \cos \theta \leq 1 \) \( \Rightarrow \frac{P_a}{P_0} > \frac{P_d}{P_0} \)
(2) Ink-bottle pores

\[ \frac{P_a}{P_0} = e^{-2s \frac{V}{RT_b}} \]

\[ \frac{P_d}{P_0} = e^{-2s \frac{V}{RT_n}} \]

\[ r_n < r_b \]

\[ \Rightarrow \quad \frac{P_a}{P_0} > \frac{P_d}{P_0} \]
uniform narrow-distributed pores

Figure 4.11 Type A hysteresis loop and possible pore structures.
Figure 4.12 Type B hysteresis loop and possible pore structures.

- **Pores between laminated plates**
- **Small neck, large body (~100nm) Pores**
Capillary condensation occurs conical, wedge-pore close at one end
BET (Brunauer-Emmett-Teller) Surface Area Measurement

Physical Adsorption of Gas Adsorbate

BET equation:

\[
\frac{P}{V_a(P_0 - P)} = \frac{1}{V_mC} + \frac{C-1}{V_mC} \left( \frac{P}{P_0} \right)
\]

(3-1)

\[C \propto \exp \left( \frac{q_1 - q_L}{RT} \right)\]

(3-2)

\[q_1 = \text{heat of adsorption of the first layer}\]
\[q_L = \text{heat of liquefication of the gas adsorbate}\]
\[V_m = \text{amount of gas adsorbed upon monolayer coverage}\]

\[s = \frac{V_m \sigma N_A}{mV_o}\]

(3-3)

\[s = \text{surface area}\]
\[\sigma = \text{mean area per molecule of the gas adsorbate}\]

\[s \left( m^2 / g \right) = \frac{4.35 \ V_m \text{ (cm}^3 \text{ at STP)}}{m(g)}\]

(3-4)
Effective BET plot is usually in the range of

\[ \frac{P}{P_0} = 0.05 \sim 0.3 \]

**Figure 3.7.** BET transform plots, each with a regression line through the linear region.
Porous Structure Determination

- Plot

Table 3.1. Data set from adsorption on reference material. Shaded area contains interpolated values.

<table>
<thead>
<tr>
<th>P/P₀</th>
<th>Vₐ</th>
<th>αₛ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0101</td>
<td>0.9613</td>
<td>0.45</td>
</tr>
<tr>
<td>0.0502</td>
<td>1.2742</td>
<td>0.60</td>
</tr>
<tr>
<td>0.1501</td>
<td>1.5902</td>
<td>0.75</td>
</tr>
<tr>
<td>0.2003</td>
<td>1.7072</td>
<td>0.81</td>
</tr>
<tr>
<td>0.4000</td>
<td>2.1156</td>
<td>1.00</td>
</tr>
<tr>
<td>0.4003</td>
<td>2.1188</td>
<td>1.00</td>
</tr>
<tr>
<td>0.5002</td>
<td>2.3421</td>
<td>1.11</td>
</tr>
<tr>
<td>0.7002</td>
<td>2.9570</td>
<td>1.40</td>
</tr>
<tr>
<td>0.7999</td>
<td>3.4895</td>
<td>1.65</td>
</tr>
<tr>
<td>0.8750</td>
<td>4.2270</td>
<td>2.00</td>
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<tr>
<td>0.8999</td>
<td>4.6219</td>
<td>2.19</td>
</tr>
<tr>
<td>0.9483</td>
<td>6.0848</td>
<td>2.90</td>
</tr>
<tr>
<td>0.9660</td>
<td>7.2637</td>
<td>3.43</td>
</tr>
<tr>
<td>0.9754</td>
<td>8.3359</td>
<td>3.94</td>
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<tr>
<td>0.9842</td>
<td>10.0120</td>
<td>4.73</td>
</tr>
<tr>
<td>0.9901</td>
<td>11.8578</td>
<td>5.61</td>
</tr>
<tr>
<td>0.9967</td>
<td>16.5133</td>
<td>7.81</td>
</tr>
</tbody>
</table>

\[ \alpha = \frac{V_a}{V_a(P/P_0 = 0.4000)} \]
Figure 3.8. $\alpha_s$ plots of experimental data showing first linear region extrapolated to the $y$-axis.
**t - Plot**

\[ t = 3.54 \left( \frac{V_a}{V_m} \right) \ \text{Å} \]

**Figure 3.9.** Idealized examples of t-Plots for (A) a microporous and (B) a mesoporous solid. Both examples show also the t-plot obtained for a nonporous sample of the same type as the porous sample.
**BJH Pore Size Distribution**

**Kelvin Equation**

\[
\ln\left(\frac{P^*}{P_0}\right) = - \left(2 \frac{\gamma}{\nu} \theta\right)/ R T r_m
\]

- \( P^* \) = the critical condensation pressure
- \( \gamma \) = the liquid surface tension
- \( \nu \) = molar volume of the condensed adsorbate
- \( \theta \) = contact angle
- \( r_m \) = mean radius of the curvature of the liquid meniscus

\[
r = r_k + t = r_m \cos \theta + t
\]

- \( r \) = pore radius
- \( t \) = thickness of adsorbate on the wall

\[
r_m = \frac{(r - t)}{\cos \theta}
\]

\[
\ln\left(\frac{P}{P_0}\right) = - \left(2 \frac{\gamma}{\nu} \cos \theta\right)/ R T (r - t)
\]

cylindrical pore
On desorption, \[ \theta \sim 0, \cos \theta \sim 1 \]

\[
\ln\left(\frac{P}{P_0}\right) = - \left(2 \theta \cos \theta \right) / RT (r - t)
\]

\[
r = - \left(2 \theta \right) / RT \ln\left(\frac{P}{P_0}\right) + t
\]

Figure 3.3. Adsorption and desorption isotherms for a porous solid.
Mercury Intrusion Porosimetry (MIP)

Resistance force due to surface tension = Force due to applied pressure

\[-p \cdot D \cdot \cos \theta = \frac{p \cdot D^2 \cdot P}{4}\]

\(P = \text{applied pressure}\)
\(D = \text{pore diameter}\)
\(\gamma = \text{surface tension of Hg}\)
\(\theta = \text{contact angle}\)

\[D = \frac{-4\gamma \cos \theta}{P}\]  \(\text{(Washburn equation)}\)

For slit-like pores

\[W = \frac{-2\gamma \cos \theta}{P}\]
\(W = \text{width between the plates}\)

\[r \sim \frac{7500}{P}\]

\(r = \text{radius} \quad \text{nm} \in \text{atm} \)

Figure 4.1. Mercury in contact with a porous solid.
**Figure 4.2.** Typical intrusion and extrusion curves from a mercury penetration analysis.

- **A:** sample of relatively coarse grains
- **B:** a single piece of material with a wide distribution of pore sizes
- **C:** fine powders without pores
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**Pore structure**- TEM
TEM photograph of Hexagonal Mesoporous Material
Synthesis of Zr-Incorporated SBA-15 Mesoporous Materials in a Self-generated Acidic Environment

Shih-Yuan Chen,† Ling-Yun Jang,‡ and Soofin Cheng*†


(a) 2M HCl

(b) No HCl

Figure 7. Morphologies of Zr–SBA-15 synthesized in solutions of different acidity. Zr/Si atomic ratio = 0.05, solvent = HCl.

Figure 8. TEM images of Zr–SBA-15 samples.
Synthesis and characterization of chiral mesoporous silica

Shunai Che\(^1\), Zheng Liu\(^2\,3\), Tetsu Ohsuna\(^3\), Kazutami Sakamoto\(^4\), Osamu Terasaki\(^3\) & Takashi Tatsumi\(^5\)

Nature (2004), 429 (6989), 281-284

Figure 3 SEM image and schematic drawings of a structural model of chiral mesoporous silica. a, SEM image, showing the microscopic features of this sample (Hitachi S-5200 SEM). The samples were observed without any metal coating. b, Schematic drawing of a structural model of the chiral mesoporous material for TEM image simulation. c, Cross-section. d, One of the chiral channels in the material.
**Figure 4** TEM images of chiral mesoporous silica: a-c. TEM images with different enlargements, showing two types of fringes (indicated by arrows and arrowheads) with different spacings. d. A simulated TEM image, showing good correspondence with the observed image. Owing to the limits on the calculation time, computer memory and image resolution, the rod diameter and the number of channels inside the rod are reduced from those observed. Images were obtained using a JEM-3010 TEM at 300 kV.

**Figure 5** Schematic drawing of chiral mesoporous silica, its TEM image and the computer-simulated TEM image. The schematic drawing a) shows the condition of the incident beam direction relative to the rod direction. The curvature of the (10) fringes can be observed in both the TEM image b) and the simulated image c). In this simulation, the angle between the incident beam direction and the perpendicular direction of the rod was 15°.
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Emission Spectrum

Continuous Spectrum

Line Spectrum
Energy Levels and Spectral Lines for Hydrogen

- **K shell**: $n = 1$
- **L shell**: $n = 2$
- **M shell**: $n = 3$
- **N shell**: $n = 4$
- **O shell**: $n = 5$
- **Ionization**

Energy levels:
- $E_1 = -B/1^2 = -2.179 \times 10^{-18} J$
- $E_2 = -B/2^2$
- $E_3 = -B/3^2$
- $E_4 = -B/4^2$
- $E_5 = -B/5^2$
- $E_\infty = 0$

Spectral series:
- Balmer series
- Paschen series
- Lyman series
Orbital Energy Diagrams

Hydrogen atom

\[ \begin{array}{cccc}
\underline{1s} & \underline{2s} & \underline{3s} & (4s, 4p, 4d, 4f) \\
\end{array} \]

A typical multielectron atom

\[ \begin{array}{cccc}
\underline{1s} & \underline{2s} & \underline{3s} & 4p \\
\underline{2p} & \underline{3p} & \underline{3d} & 4s \\
\end{array} \]
Atomic Emission Spectra of Some Elements
Inductively Coupled Plasma (ICP)

- Excitation of the Sample for Elemental Analysis

**Figure 10-1** A typical inductively coupled plasma. (From V. A. Fussel, Science, 1978, 202, 186. With permission. Copyright 1978 by the American Association for the Advancement of Science.)

**Figure 10-2** A typical nebulizer for sample injection into a plasma source. (From V. A. Fussel, Science, 1978, 202, 186. With permission. Copyright 1978 by the American Association for the Advancement of Science.)
The molar ratios of Cu and T-atoms in CuAPO-5 analyzed by ICP-AES.

<table>
<thead>
<tr>
<th>Element</th>
<th>AlPO$_4$-5</th>
<th>0.5% CuAPO$_4$-5</th>
<th>1% CuAPO$_4$-5</th>
<th>2% CuAPO$_4$-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0 (0%)</td>
<td>0.01 (0.50%)</td>
<td>0.02 (1.00%)</td>
<td>0.04 (1.96%)</td>
</tr>
<tr>
<td>P</td>
<td>1 (50%)</td>
<td>1 (49.75%)</td>
<td>1 (49.5%)</td>
<td>1 (49.02%)</td>
</tr>
<tr>
<td>Al</td>
<td>1 (50%)</td>
<td>1 (49.75%)</td>
<td>1 (49.5%)</td>
<td>1 (49.02%)</td>
</tr>
<tr>
<td>ICP-AES</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0 (0%)</td>
<td>0.008 (0.38%)</td>
<td>0.017 (0.81%)</td>
<td>0.032 (1.53%)</td>
</tr>
<tr>
<td>P</td>
<td>0.99 (49.8%)</td>
<td>1.06 (51.3%)</td>
<td>1.07 (51.3%)</td>
<td>1.06 (50.67%)</td>
</tr>
<tr>
<td>Al</td>
<td>1 (50.2%)</td>
<td>1 (48.4%)</td>
<td>1 (47.9%)</td>
<td>1 (47.80%)</td>
</tr>
</tbody>
</table>

Values in parentheses are molar percentages of Cu and T-atoms.
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The Photoelectric Effect

Albert Einstein considered electromagnetic energy to be bundled in to little packets called photons. Energy of photon = \( E = hv \)

- Photons of light hit surface electrons and transfer their energy

\[ hv = \text{B.E.} + \text{K.E.} \]

- The energized electrons overcome their attraction and escape from the surface

Photoelectron spectroscopy detects the kinetic energy of the electron escaped from the surface.

- XPS – X-ray as the light source, core electrons escaped
- UPS – UV as the light source, valence electrons escaped
Figure 3.2: Photoemission and the Auger process. Left: An incident X-ray photon is absorbed and a photoelectron emitted. Measurement of its kinetic energy allows one to calculate the binding energy of the photoelectron. The atom stays behind as an unstable ion with a hole in one of the core levels. Right: The excited ion relaxes by filling the core hole with an electron from a higher shell. The energy released by this transition is taken up by another electron, the Auger electron, which leaves the sample with an elementspecific kinetic energy. In Auger spectroscopy the initial core holes are created by a beam of energetic (2-5 keV) electrons.

\[ E_k = h\nu - E_b - \phi \]

\[ \varphi = \text{work function} \]

\[ E_k(KL_1 L_2) = [E_b(K) - E_b(L_1)] - E_b(L_2) - \varphi \]
Figure 3.1: The mean free path of an electron depends on its kinetic energy and determines how much surface information it carries. Optimum surface sensitivity is obtained with electrons in the 25 - 200 eV range (from Somorjai, [16]).
**Figure 3.3:** XPS spectrum of a Rh/Al$_2$O$_3$ model catalyst prepared by impregnating a thin film of Al$_2$O$_3$ on aluminum with a solution of RhCl$_3$ in water (courtesy of L.C.A. van den Oetelaar, Eindhoven).
Figure 3.4: XPS scans between 0 and 450 eV of two organoplatinum complexes showing peaks due to Pt, Cl, N and C. The C 1s signal not only represents carbon in the compound but also contaminant hydrocarbon fragments, as on any sample. The abbreviation 'Me' in the structures stands for CH₃ (courtesy of J.C. Muijsers, Eindhoven).
Figure 3.5: Pt 4f XPS spectra
TABLE II

Details of the Supported Metal Systems Studies Presented in Fig. 2

<table>
<thead>
<tr>
<th>Curve (Fig. 2)</th>
<th>Metal and electron</th>
<th>$BE^a$ for bulk (eV)</th>
<th>Support</th>
<th>Reference$^b$</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Pd 3$d_{5/2}$</td>
<td>335.0</td>
<td>C</td>
<td>a</td>
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<tr>
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<td>Y-Zeolite</td>
<td>b</td>
</tr>
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<td>3</td>
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<td>SiO$_2$</td>
<td>c</td>
</tr>
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<tr>
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$^a$ BE = binding energy; $\Delta BE = BE$(observed) – BE(bulk).

FIG. 2. Binding energy shifts $\Delta BE$ of metal core levels measured by photoelectron spectroscopy (XPS) versus fraction exposed FE and mean particle size $\bar{d}$ for various supported metal systems (see Table II for details of the studies).