Lecture Note #1 (Spring, 2020)

Introduction to surface & interface

1. Introduction to lecture (syllabus)
2. Introduction to surface and interface

Reading: Kolasinski, Introduction

2020 Spring
458-622 Advanced Surface Chemistry, 표면화학특론

LECTURER: Professor Yung-Eun Sung (성영은)
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OUTLINE

This class deals with basic principles of surface and interface at solid and liquid. Those include structures and adsorbates, experimental techniques, thermodynamics & kinetics on surface, liquid interfaces, and application to catalysis, electrocatalysis, and nanoscience.

TEXTBOOKS

Kurt W. Kolasinski, Surface Science – Foundations of Catalysis and Nanoscience (4th edition), Wiley. 2020. (3rd ed or old Versions OK) (e-book(3rd ed) available in SNU Library)

REFERENCES

G. A. Somorjai, Introduction to Surface Chemistry and Catalysis, John Wiley. (e-Book available in SNU Library)
Duncan J. Shaw, Introduction to Colloid and Surface Chemistry, John Wiley.
(Korean reference: 임재석, 임굉, 콜로이드과학 및 표면화학, 내하출판사, 2015)

SCHEDULES (online lectures in first several weeks**)**

1. Introduction to Surface & Interface (Introduction) (1 week)
2. Surface and Adsorbate Structure (ch.1) (1-3 weeks)
3. Experimental Probes and Techniques (ch.2) (4-5 weeks)
4. Chemisorption, Physisorption and Dynamics (ch.3) (6-7 weeks)
5. Thermodynamics and Kinetics of Adsorption and Desorption (ch.4) (8-9 weeks)
6. Thermodynamics of Surface and Interface (ch.5) (10-11 weeks)
7. Liquid Interfaces (ch.5) (12-13 weeks)
8. Application to Catalysis and Nanoscience (ch.6, 7, 8) (14-15 week)

GRADING (≥B$^+$ <80%) Midterm Exam 40%, Final Exam 40%, Homeworks & Attendance 20 %

LECTURE ROOM & TIME: Rm #302-409, 11:00-12:15 Mon. & Wed.
Make-up lecture: May 23(Sat) 11:00~13:45

OFFICE HOUR: Rm #302-729, 13:00-16:00 Mon. & Wed.

TA: Jin Ki Kwak(곽진기), Rm#302-1007, Tel: 880-9123, 010-7231-2340,
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History of surface science

Early 1800s

- Spontaneous spreading of oil on water: Benjamin Franklin
- Platinum-surface-catalyzed reaction of H_2 & O_2 in 1823 (Dobereiner): portable flame ("lighter")
- Discovery of heterogeneous catalysis by 1835: Kirchhoff, Davy, Henry, Philips, Faraday, Berzelius
- Photography by 1835: Daguerre process
- Study of tribology or friction

1860-1912

- Surface-catalyzed chemistry-based technologies: Deacon process ($2HCl + O_2 \rightarrow H_2O + Cl_2$), SO_2 oxidation to SO_3 (Messel, 1875), CH_4 reaction with steam to CO & H_2 (Mond, 1888), NH_3 oxidation (Ostwald, 1901), C_2H_4 hydrogenation (Sabatier, 1902), NH_3 synthesis (Haber, Mittasch, 1905-12)
- Surface tension measurement → thermodynamics of surface phases (Gibbs, 1877)
- Colloids (Graham, 1861), micelles (Nageli), metal colloids (Faraday) → paint industry, artificial rubber in early 20th century

Early 20th century

- Light bulb filament, high-surface-area gas absorbers in the gas mask, gas-separation technologies → atomic & molecular adsorption (Langmuir, 1915)
- Studies of electrode surface in electrochemistry (from 19th century)
- Surface diffraction of electrons (Davisson & Germer, 1927)
- Surface studies: Germany (Haber, Polanyi, Farkas, Bonhoefer), UK (Rideal, Roberts, Bowden), USA (Langmuir, Emmett, Harkins, Taylor, Ipatief, Adams), and other countries

After 1950s & 2000s

- Gas-phase molecular process on the molecular level
- Ultra high vacuum (UHV) system
- Surface characterization techniques
- Scanning tunneling microscope(STM, Binning & Rohrer,1983) (Nobel Prize in 1986): atomic scale image & manipulation
- Graphene (Novoselov & Geim, 2004) (Nobel Prize in 2010)
- Nobel Prize in 2007 to Gerhard Ertl for “chemical processes on solid surfaces”
- Nanotechnology in 2000’s

Why this coursework?

Surfaces and interfaces

- Surface: interface between immiscible bodies
- Outer space: solid-vacuum interface
- Surfaces on earth are exposed to another solid or gas or liquid → interface: *s/s, s/l, s/g, l/l. l/g*

Chemical engineering, inorganic, semiconductor, nanotechnology, electrochemistry, materials, organic, polymer, biological applications

Polymer surfaces

- Surface is very different from bulk due to structural unit connected covalent chemical bonds

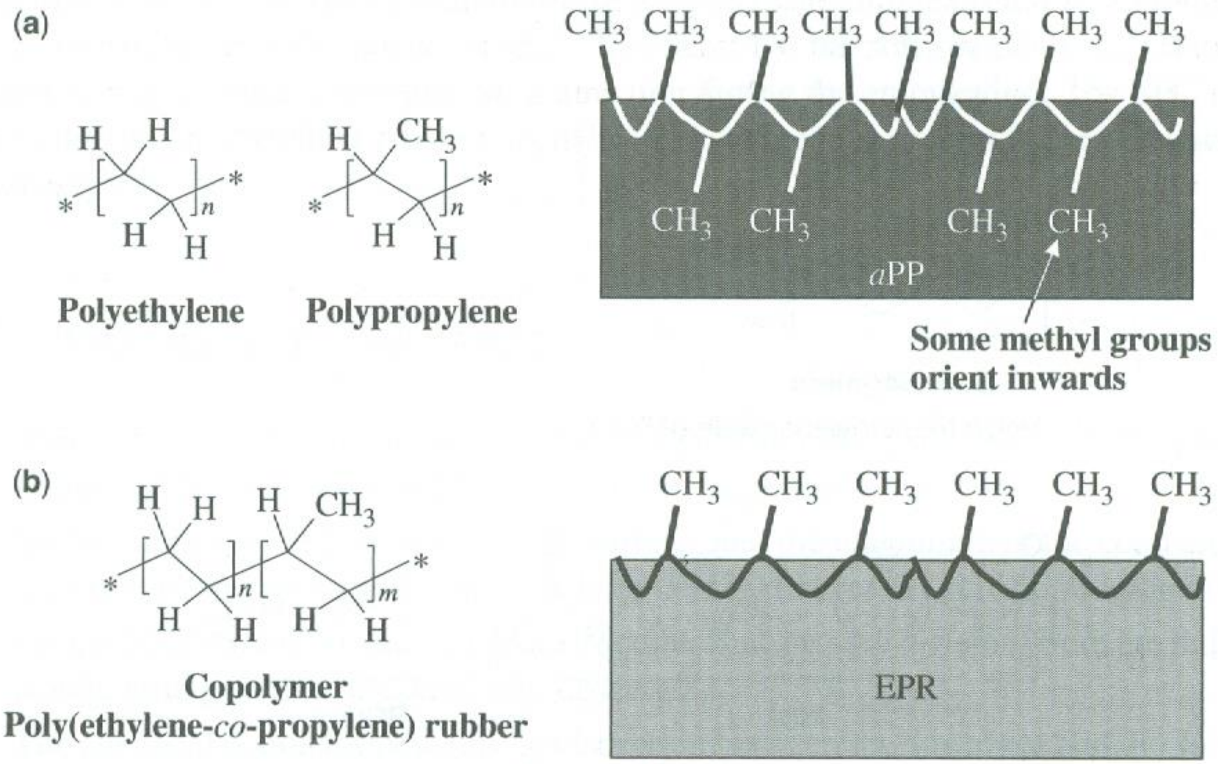
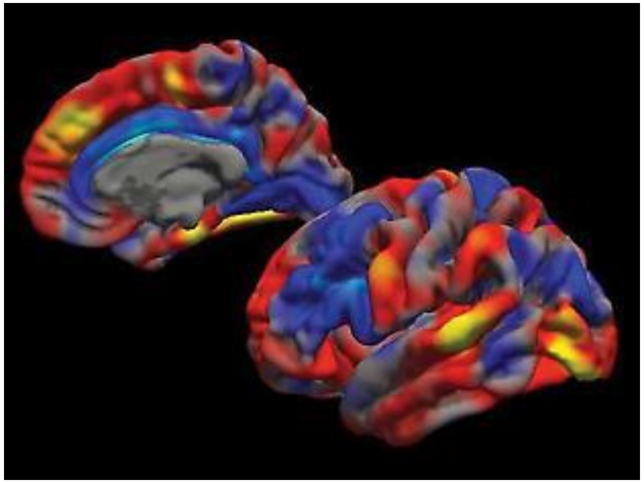


Figure 2.38. (a) Structure of polyethylene, polypropylene, and their copolymer, poly(ethylene-*co*-propylene) rubber (EPR). (b) Schematic for the orientation of surface CH_3 groups on the atactic polypropylene (*a*PP) and the EPR.

Somorjai, Introduction to Surface Chemistry and Catalysis

Biological surfaces



Brain

australasianscience.com.au

Leaf

Sea urchin(성게)

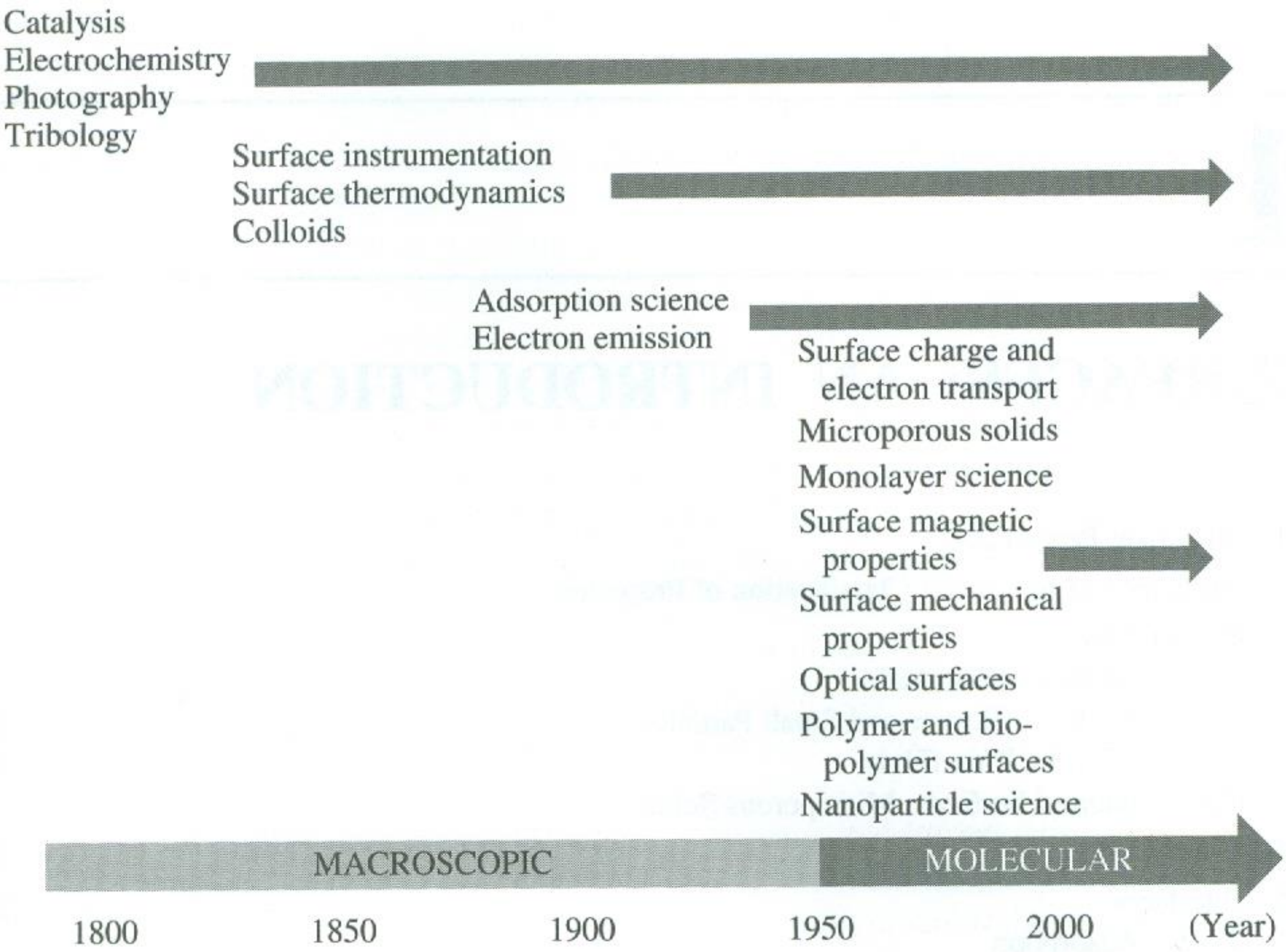


Figure 1.1. Timeline of the historical development of surface chemistry.

Somorjai, Introduction to Surface Chemistry and Catalysis

The techniques of surface science

- AES, AFM, EELS, ESCA, EXAFS, FEM, FIM, FTIR, HEIS, HPXPS, HREELS, IRAS, ISS, LEED, LEIS, NEXAFS, NMR, RBS, SERS, SEXAFS, SFG, SHG, SIMS, STM, TEM, TDS, UPS, XANES, SPS, XRD… (see Table 1.1)

- Surface properties: structure, composition, oxidation states, chemical properties, electronic properties, mechanical properties → atomic resolution, smaller energy resolution, shorter time scales, in situ, high pressure

- Sources: electrons, atoms, ions, photons

Interfaces

- On earth, surfaces are always covered with a layer of atoms or molecules → interfaces

  s/g, s/l, l/l, s/s/ l/g

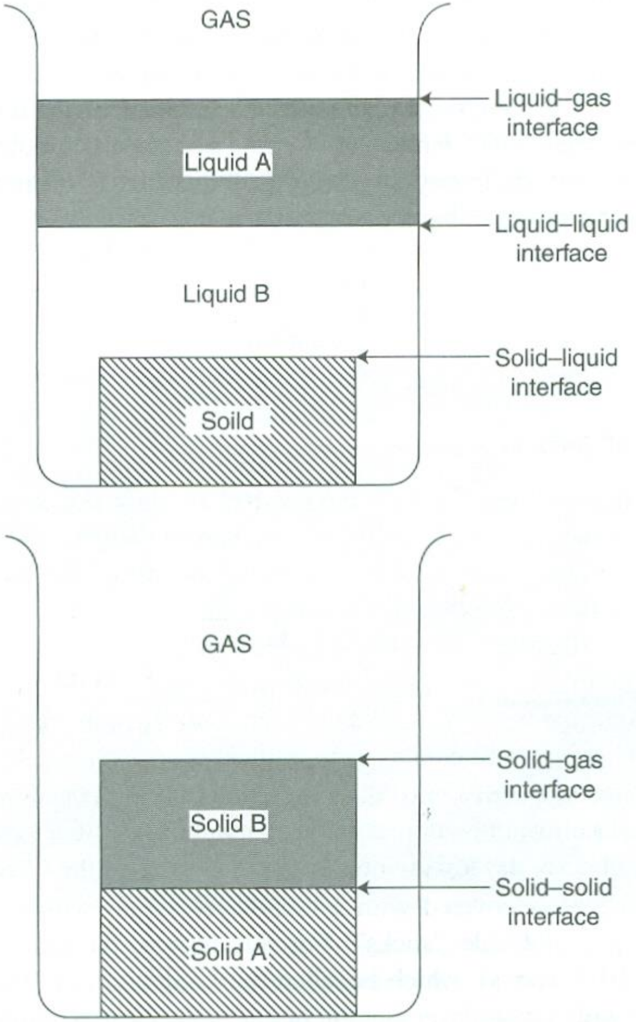


Figure 1.12. Schematic diagram of interfaces (e.g., solid–liquid, liquid–liquid, liquid–gas, solid–solid, and solid–gas interfaces).

Somorjai, Introduction to Surface Chemistry and Catalysis

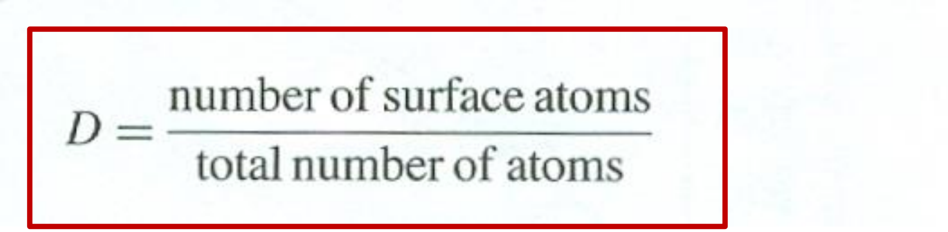
External surfaces

- Surface concentration → estimated from the bulk density

  molecular density per cm^3, ρ → surface concentration per cm^2, $\sigma = \rho^{2/3}$
  e.g., 1 g/cm^3 → $\rho \sim 5 \times 10^{22}$ → $\sigma \sim \underline{10^{15}\text{ molecules cm}^{-2}}$ ($10^{19}/\text{m}^2$)

- Clusters and small particles

  Dispersion



$$\boxed{D = \frac{\text{number of surface atoms}}{\text{total number of atoms}}} \qquad (1.1)$$

Somorjai

volume of cluster ~d^3, surface area ~ d^2 → D ~ 1/d (inverse of the cluster size)

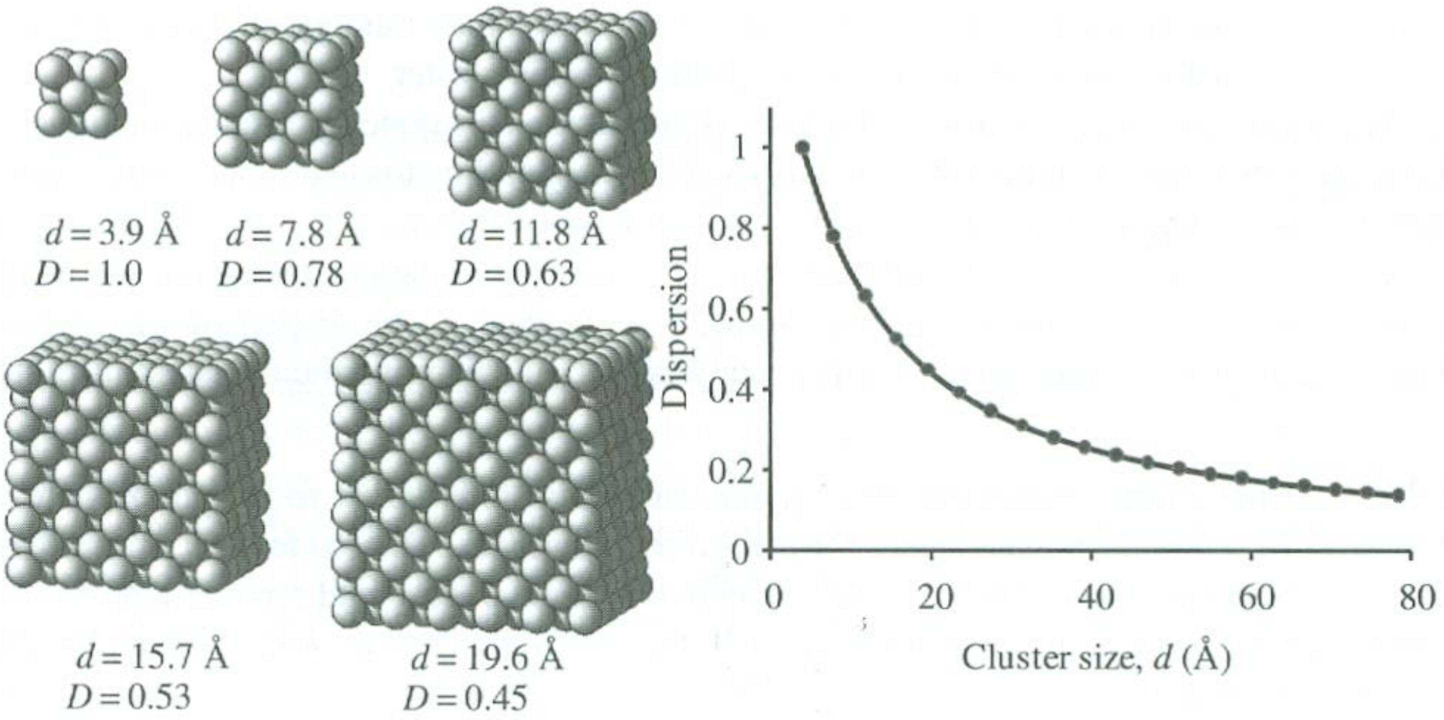


Figure 1.7. Cubic clusters with the face-centered cubic (fcc) packing of 14, 50, 110, 194, and 302 atoms (the left panel). In the smallest cluster, all of the atoms are on the surface. However, the dispersion defined as the number of surface atoms divided by the total number of atoms in the cluster, declines rapidly with increasing cluster size, which is shown in the right panel of the figure. The size d is the length of the edge of the cubic clusters. The lattice constant of the fcc clusters is assumed to be 3.9 Å, which is close to that of the Pt crystal.

10 nm radius → 10^{-3} surface

Somorjai, Introduction to Surface Chemistry and Catalysis

- D depends somewhat on the shape of the particle and how the atoms are packed: the spherical cluster has smaller surface area than the cube cluster → lower dispersion (D) in round shape

- Higher D in catalysts → higher surface, lower the material cost

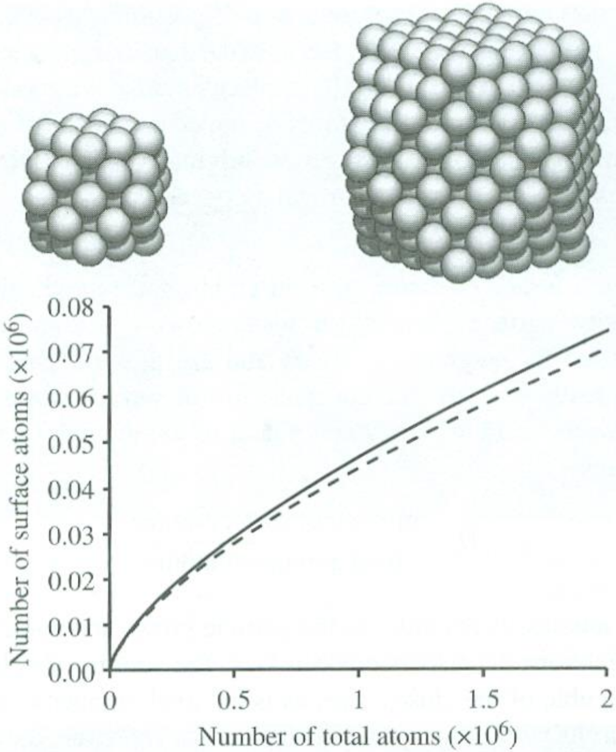


Figure 1.8. Truncated cubic clusters with the fcc packing of 55 and 309 atoms (the upper panel). The lower panel shows the number of surface atoms as a function of the total number of atoms for the cubic cluster (the solid line) and the truncated cubic cluster (the dashed line). Compared to the cubic cluster, the truncated cubic cluster is relatively rounder, so it has fewer atoms on the surface.

Brain
Leaf for photosynthesis
Sea urchin(성게)

Somorjai

- Thin films: of great importance to many real-world problems and surface science

Internal surfaces: microporous solids

- Clays, graphite: layers → intercalation (for battery, filter, absorbent etc)
- Zeolites, MOFs(metal-organic frameworks): ordered cages of molecular dimensions → large surface area

Surface science & catalysis

- Catalysis: basis of chemical industry → billions of dollars of economic activity
- “Catalysis”, Greek “wholly loosening” (κατα + λνσις): it takes part in a reaction but is not consumed → changing activation barrier → speed up a reaction (but, not change equilibrated state) & perform selectively for the desired product

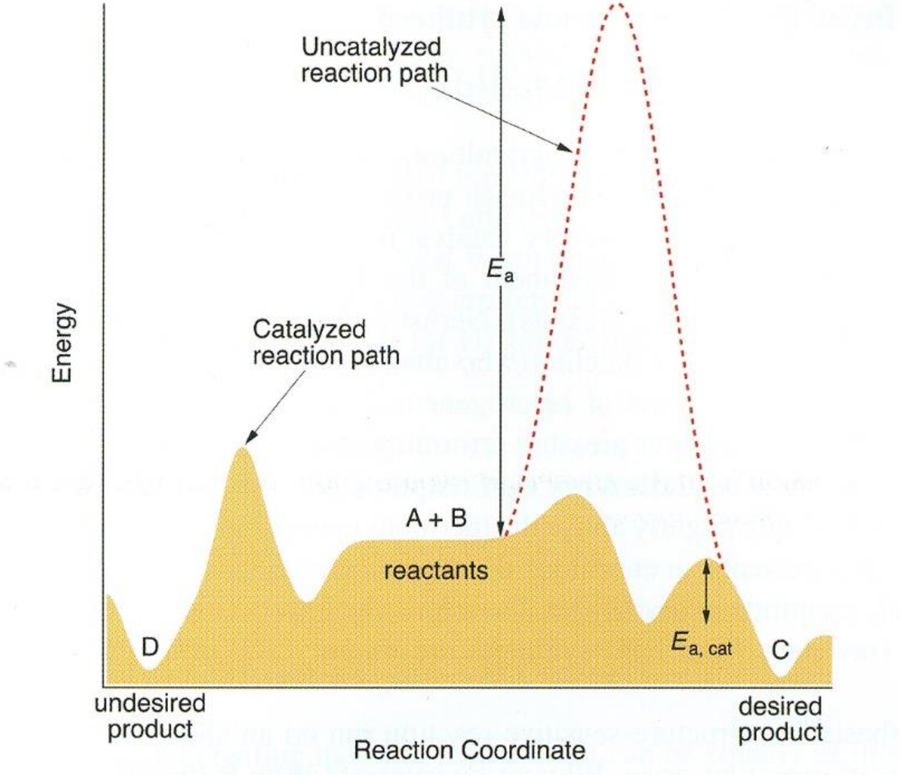
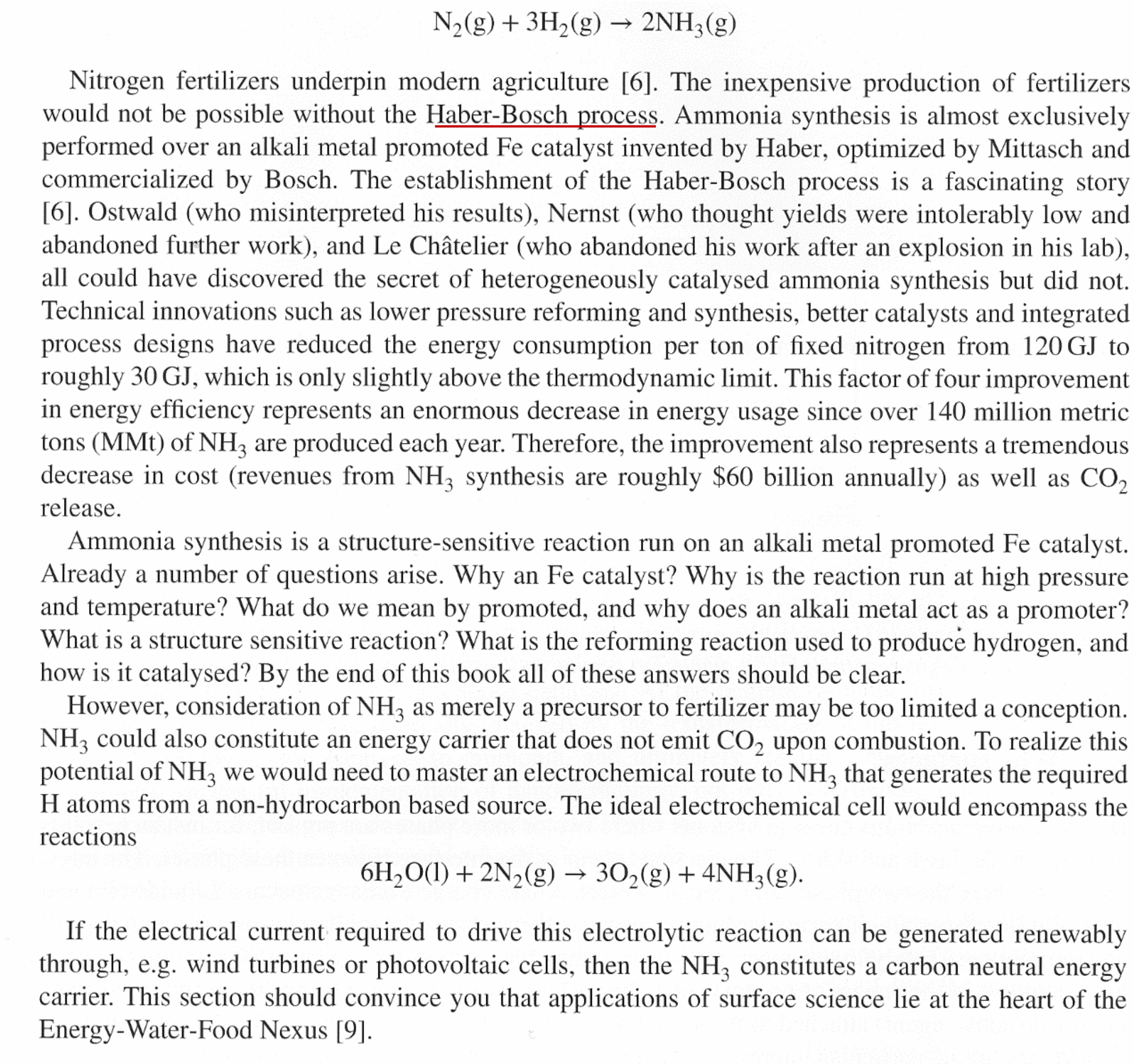


Fig.1.2. Kolasinski

Why surfaces and interfaces?

- Ammonia synthesis



$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Nitrogen fertilizers underpin modern agriculture [6]. The inexpensive production of fertilizers would not be possible without the Haber-Bosch process. Ammonia synthesis is almost exclusively performed over an alkali metal promoted Fe catalyst invented by Haber, optimized by Mittasch and commercialized by Bosch. The establishment of the Haber-Bosch process is a fascinating story [6]. Ostwald (who misinterpreted his results), Nernst (who thought yields were intolerably low and abandoned further work), and Le Châtelier (who abandoned his work after an explosion in his lab), all could have discovered the secret of heterogeneously catalysed ammonia synthesis but did not. Technical innovations such as lower pressure reforming and synthesis, better catalysts and integrated process designs have reduced the energy consumption per ton of fixed nitrogen from 120 GJ to roughly 30 GJ, which is only slightly above the thermodynamic limit. This factor of four improvement in energy efficiency represents an enormous decrease in energy usage since over 140 million metric tons (MMt) of NH_3 are produced each year. Therefore, the improvement also represents a tremendous decrease in cost (revenues from NH_3 synthesis are roughly $60 billion annually) as well as CO_2 release.

Ammonia synthesis is a structure-sensitive reaction run on an alkali metal promoted Fe catalyst. Already a number of questions arise. Why an Fe catalyst? Why is the reaction run at high pressure and temperature? What do we mean by promoted, and why does an alkali metal act as a promoter? What is a structure sensitive reaction? What is the reforming reaction used to produce hydrogen, and how is it catalysed? By the end of this book all of these answers should be clear.

However, consideration of NH_3 as merely a precursor to fertilizer may be too limited a conception. NH_3 could also constitute an energy carrier that does not emit CO_2 upon combustion. To realize this potential of NH_3 we would need to master an electrochemical route to NH_3 that generates the required H atoms from a non-hydrocarbon based source. The ideal electrochemical cell would encompass the reactions

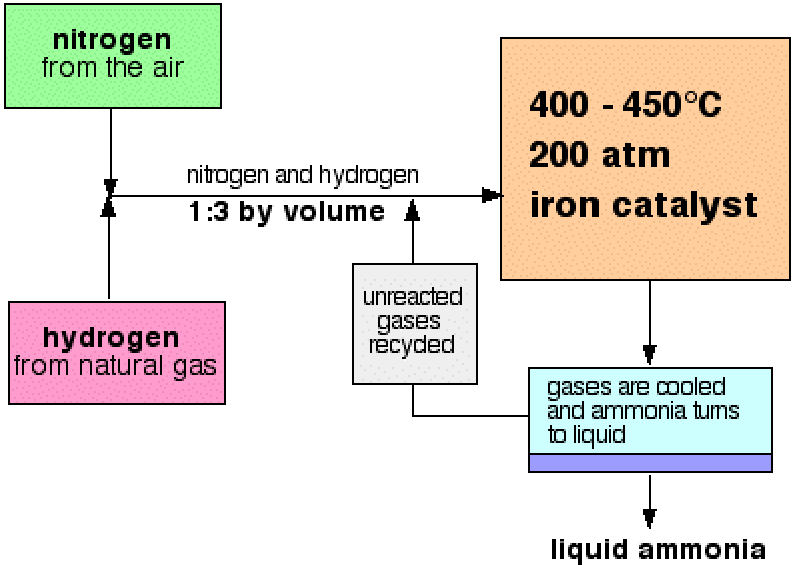
$$6H_2O(l) + 2N_2(g) \rightarrow 3O_2(g) + 4NH_3(g).$$

If the electrical current required to drive this electrolytic reaction can be generated renewably through, e.g. wind turbines or photovoltaic cells, then the NH_3 constitutes a carbon neutral energy carrier. This section should convince you that applications of surface science lie at the heart of the Energy-Water-Food Nexus [9].

NH_3: a carbon neutral energy carrier

Kolasinski

Haber Process



nitrogen
from the air

hydrogen
from natural gas

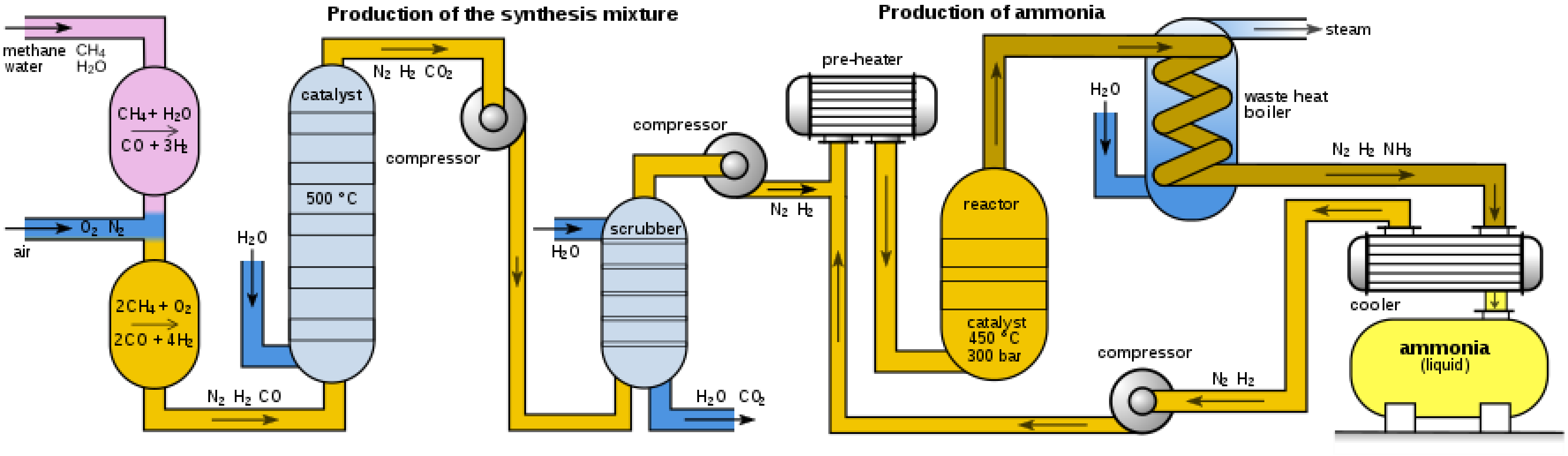
nitrogen and hydrogen
1 :3 by volume

400 - 450°C
200 atm
iron catalyst

unreacted gases recycled

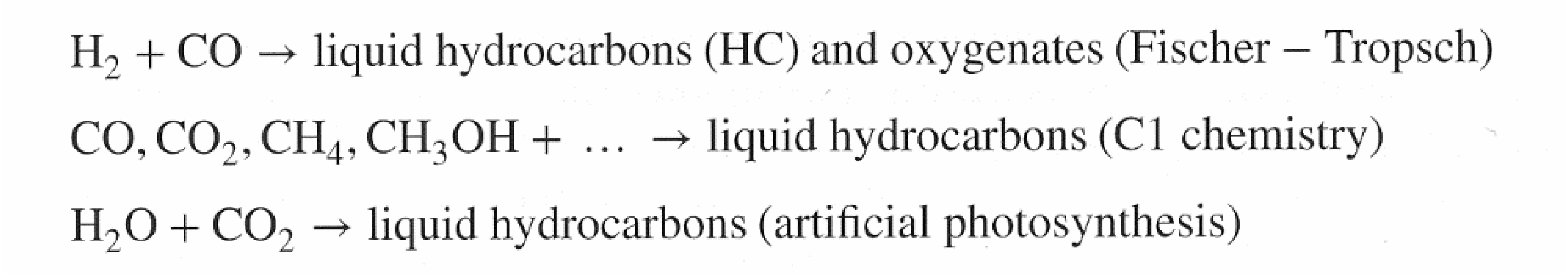
gases are cooled and ammonia turns to liquid

liquid ammonia



From Wikipedia

- Gas-to-liquids: Fischer-Tropsch synthesis, C1 chemistry, artificial photosynthesis



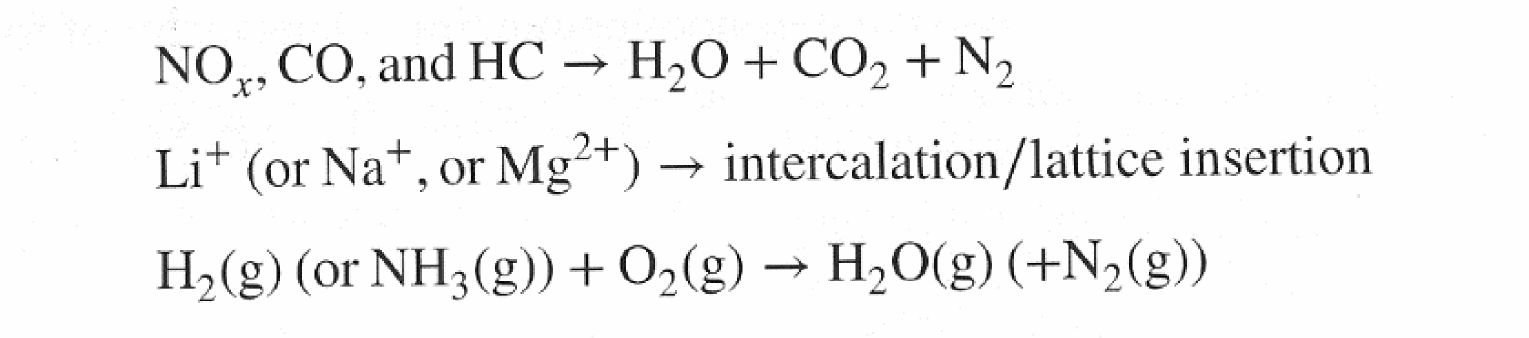
$$H_2 + CO \rightarrow \text{liquid hydrocarbons (HC) and oxygenates (Fischer – Tropsch)}$$

$$CO, CO_2, CH_4, CH_3OH + \ \ldots \ \rightarrow \text{liquid hydrocarbons (C1 chemistry)}$$

$$H_2O + CO_2 \rightarrow \text{liquid hydrocarbons (artificial photosynthesis)}$$

-Transforming natural gas & coal
-Biomass
-Artificial photosynthesis: a branch of photocatalysis, H_2 production, CO_2 conversion, solar fuels

- Clean propulsion: three-way catalyst, batteries, fuel cells



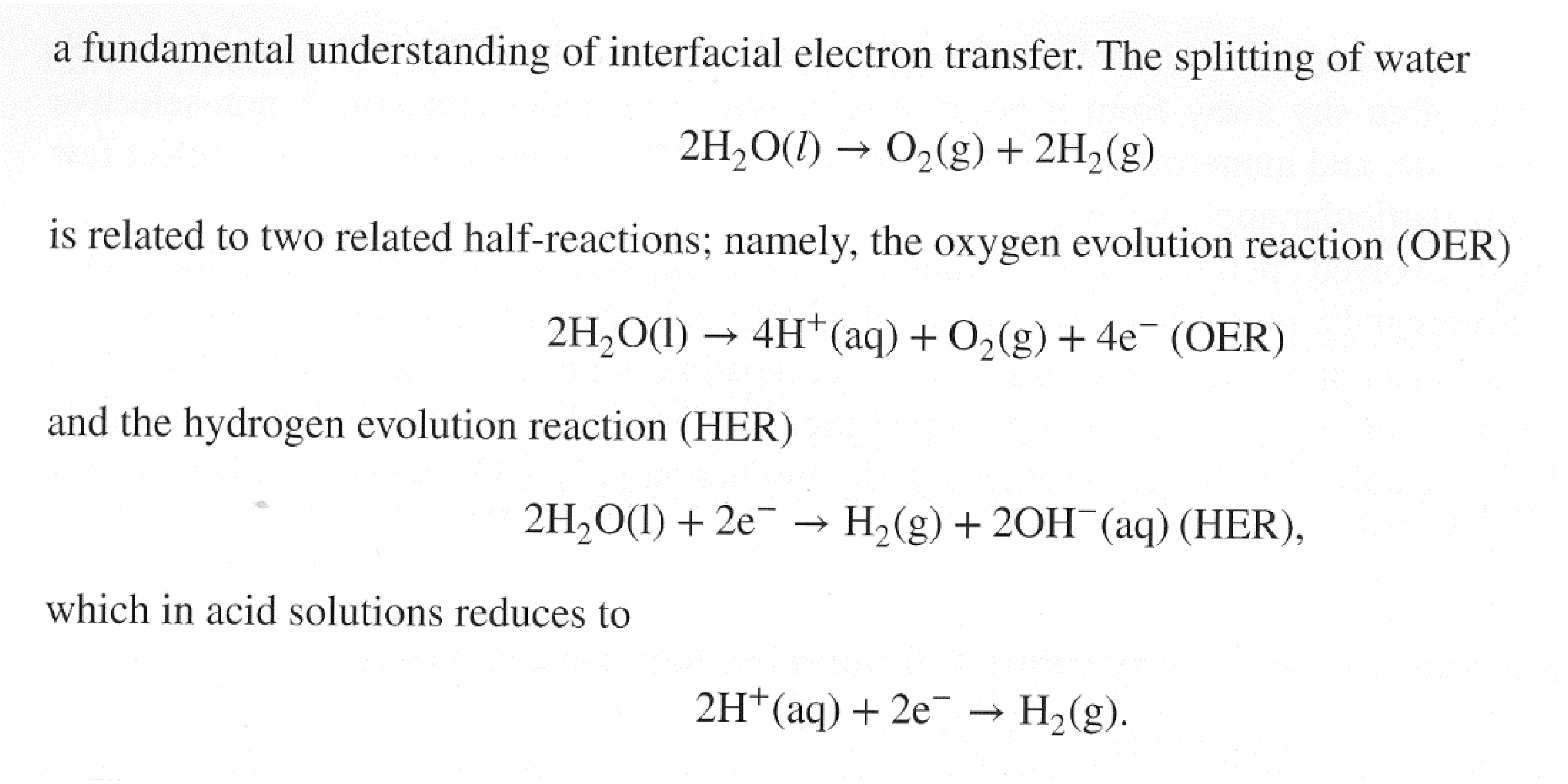
$$\mathrm{NO}_x,\ \mathrm{CO},\ \text{and HC} \rightarrow \mathrm{H_2O} + \mathrm{CO_2} + \mathrm{N_2}$$

$$\mathrm{Li}^+\ (\text{or } \mathrm{Na}^+,\ \text{or } \mathrm{Mg}^{2+}) \rightarrow \text{intercalation/lattice insertion}$$

$$\mathrm{H_2(g)}\ (\text{or } \mathrm{NH_3(g)}) + \mathrm{O_2(g)} \rightarrow \mathrm{H_2O(g)}\ (+\mathrm{N_2(g)})$$

-reduce pollution, (ultra)fine particle (PM 2.5, particulate matter)
-batteries, photovoltaics, fuel cells, thermoelectrics: surface, interface, pores

- Water splitting: oxygen and hydrogen evolution reaction (OER, HER)



a fundamental understanding of interfacial electron transfer. The splitting of water

$$2H_2O(l) \rightarrow O_2(g) + 2H_2(g)$$

is related to two related half-reactions; namely, the oxygen evolution reaction (OER)

$$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^- \text{ (OER)}$$

and the hydrogen evolution reaction (HER)

$$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \text{ (HER)},$$

which in acid solutions reduces to

$$2H^+(aq) + 2e^- \rightarrow H_2(g).$$

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- Semiconductor processing and nanotechnology

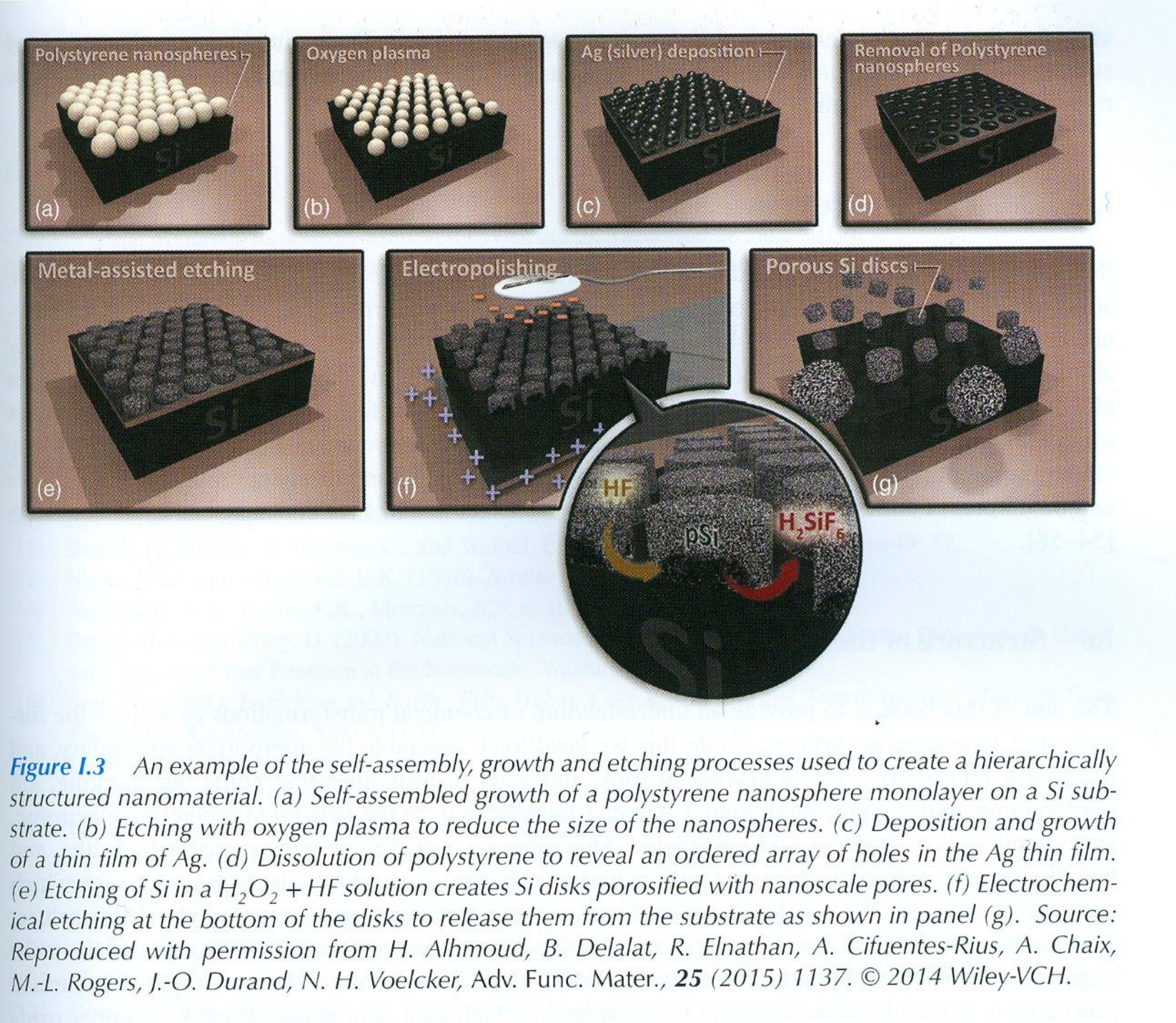

Figure I.3 *An example of the self-assembly, growth and etching processes used to create a hierarchically structured nanomaterial. (a) Self-assembled growth of a polystyrene nanosphere monolayer on a Si substrate. (b) Etching with oxygen plasma to reduce the size of the nanospheres. (c) Deposition and growth of a thin film of Ag. (d) Dissolution of polystyrene to reveal an ordered array of holes in the Ag thin film. (e) Etching of Si in a* $H_2O_2 + HF$ *solution creates Si disks porosified with nanoscale pores. (f) Electrochemical etching at the bottom of the disks to release them from the substrate as shown in panel (g). Source: Reproduced with permission from H. Alhmoud, B. Delalat, R. Elnathan, A. Cifuentes-Rius, A. Chaix, M.-L. Rogers, J.-O. Durand, N. H. Voelcker,* Adv. Func. Mater., **25** *(2015) 1137. © 2014 Wiley-VCH.*

Large interface-to-volume ratio

Kolasinski

Structure of coursework

Surface and Adsorbate Structure: geometric, electronic, vibrational

Experimental Probes and Techniques

Chemisorption, Physisorption and Dynamics

Thermodynamics and Kinetics of Adsorption and Desorption

Thermodynamics of Surface and Interface

Liquid Interfaces: surfactant an so on

Application to Catalysis and Nanoscience