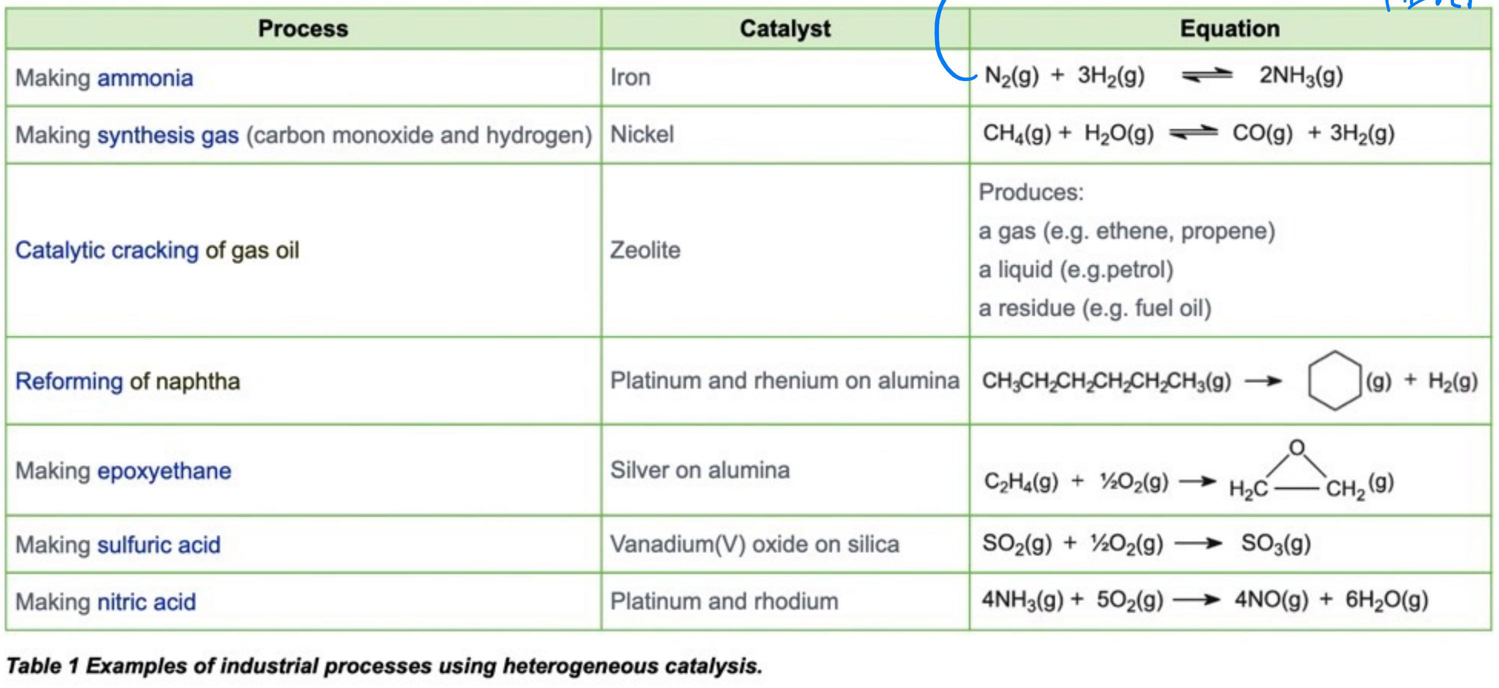
CBE 40445

9/16/20

HETEROGENEOUS CATALYSIS

SOME REVIEW

ΔH = −92 KJ/MOLE AT RXN TEMP

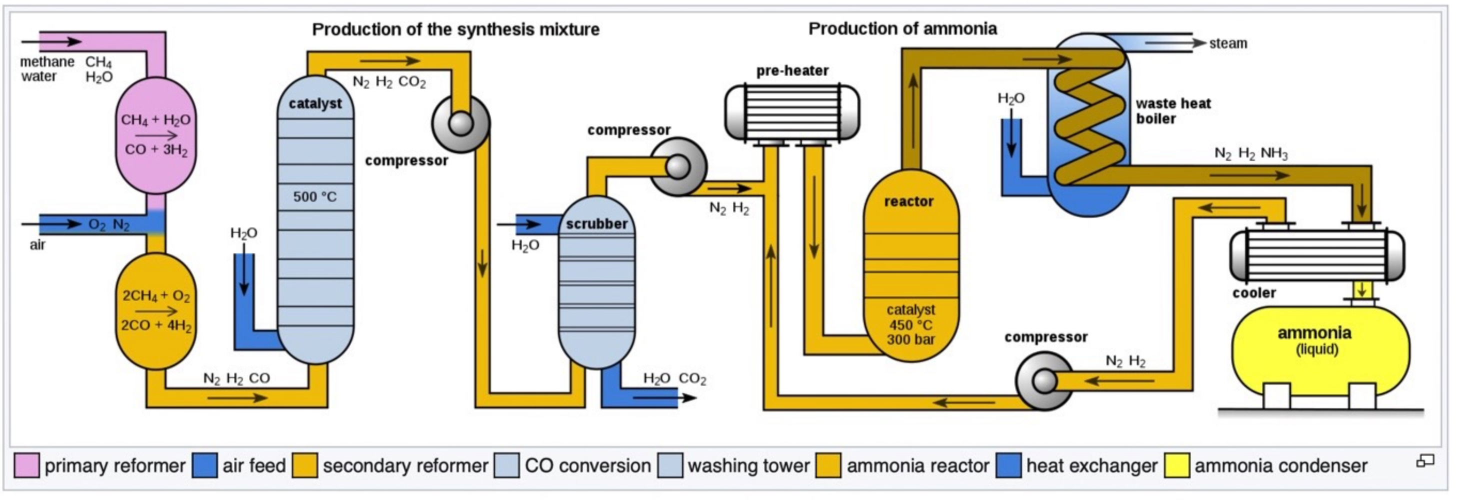


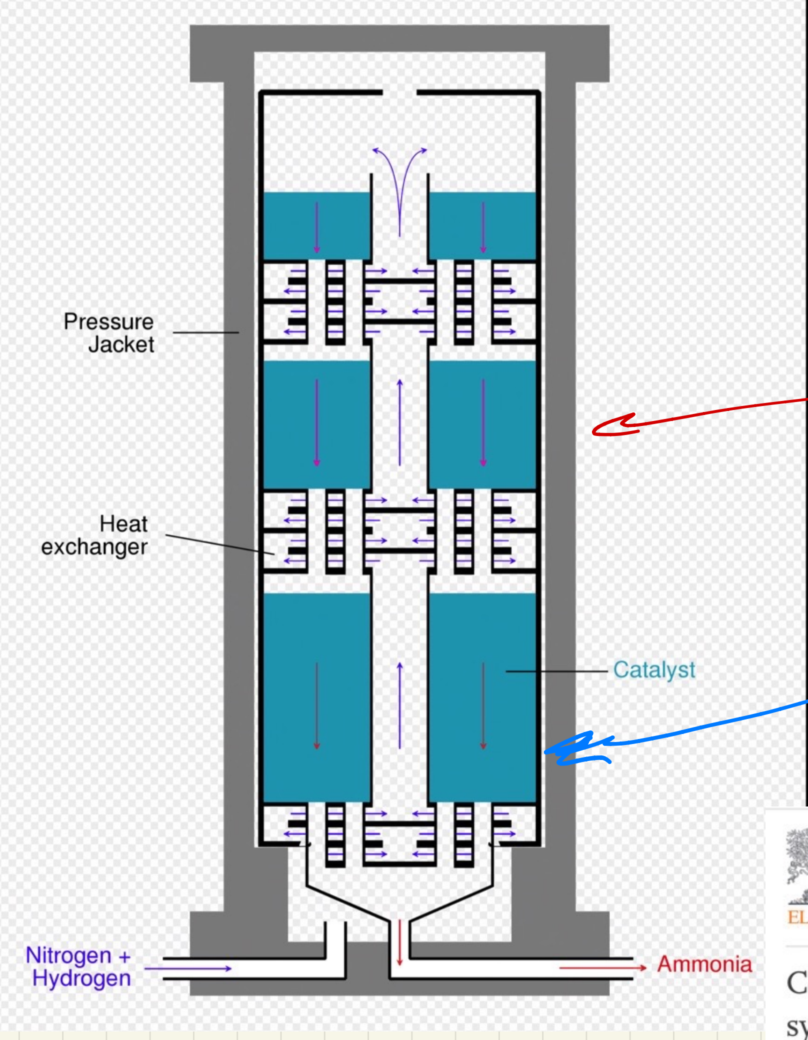
Process	Catalyst	Equation
Making **ammonia**	Iron	$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
Making **synthesis gas** (carbon monoxide and hydrogen)	Nickel	$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$
Catalytic cracking of gas oil	Zeolite	Produces: a gas (e.g. ethene, propene) a liquid (e.g.petrol) a residue (e.g. fuel oil)
Reforming of naphtha	Platinum and rhenium on alumina	$CH_3CH_2CH_2CH_2CH_2CH_3(g) \longrightarrow$ (g) + $H_2(g)$
Making **epoxyethane**	Silver on alumina	$C_2H_4(g) + ½O_2(g) \longrightarrow \overset{O}{H_2C—CH_2}(g)$
Making **sulfuric acid**	Vanadium(V) oxide on silica	$SO_2(g) + ½O_2(g) \longrightarrow SO_3(g)$
Making **nitric acid**	Platinum and rhodium	$4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

Table 1 Examples of industrial processes using heterogeneous catalysis.

https://www.essentialchemicalindustry.org/processes/catalysis-in-industry.html

FROM WIKIPEDIA





T ~ 350 C

P ~ 200 ATM

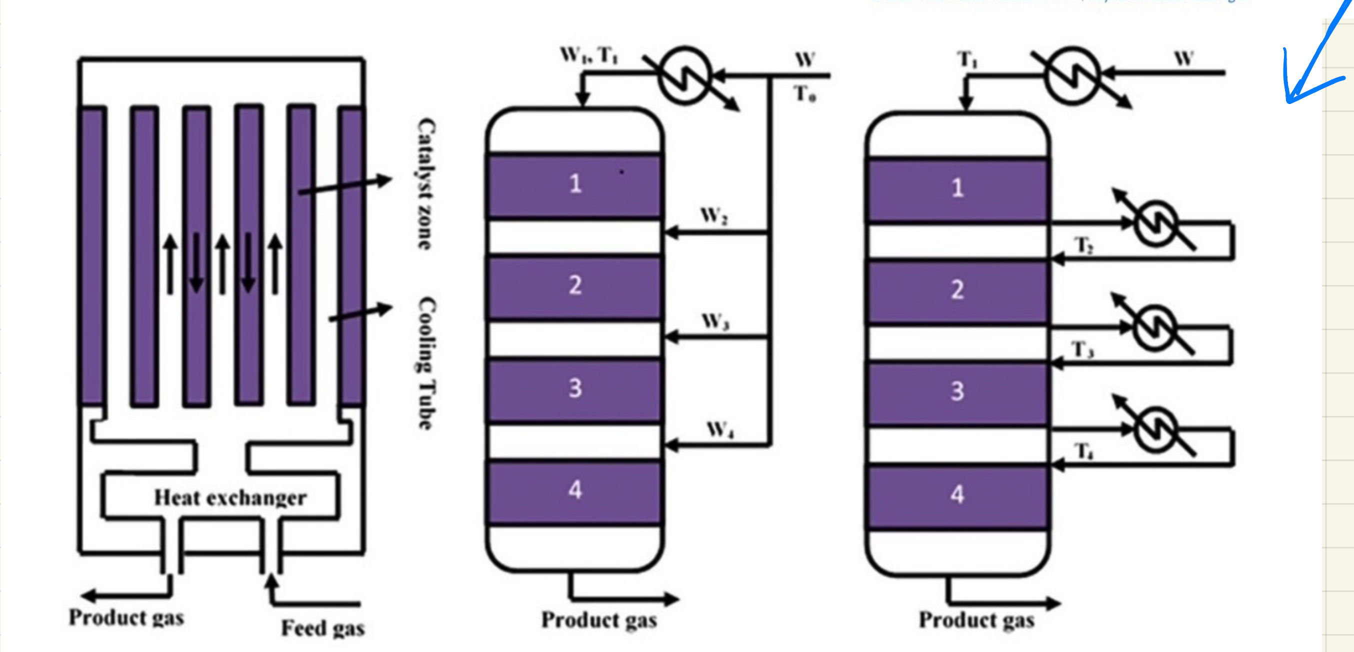
HIGHLY EXOTHERMIC

APPROACHES EQUILIBRIUM

Chemical Engineering Research and Design
Volume 128, December 2017, Pages 306-317

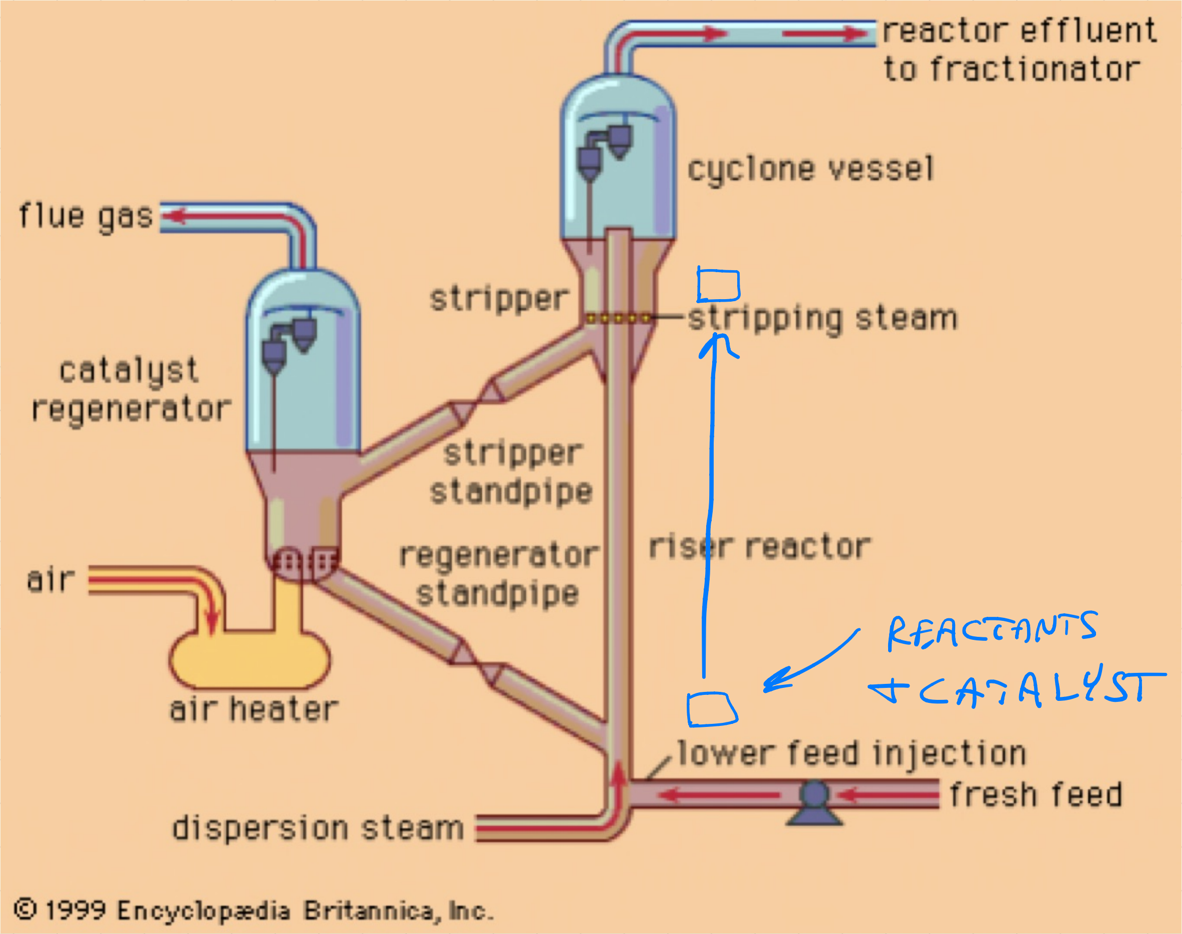
Comparison between three types of ammonia synthesis reactor configurations in terms of cooling methods

Mohammad Hasan Khademi, Reyhaneh Sadat Sabbaghi



Internal direct cooling reactor, IDCR) (Adiabatic quench cooling reactor, AQCR) (Adiabatic indirect cooling reactor, AICR)

CATALYTIC CRACKING



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$$C_{12}H_{26} \rightarrow C_5 + C_6$$

ENDOTHERMIC

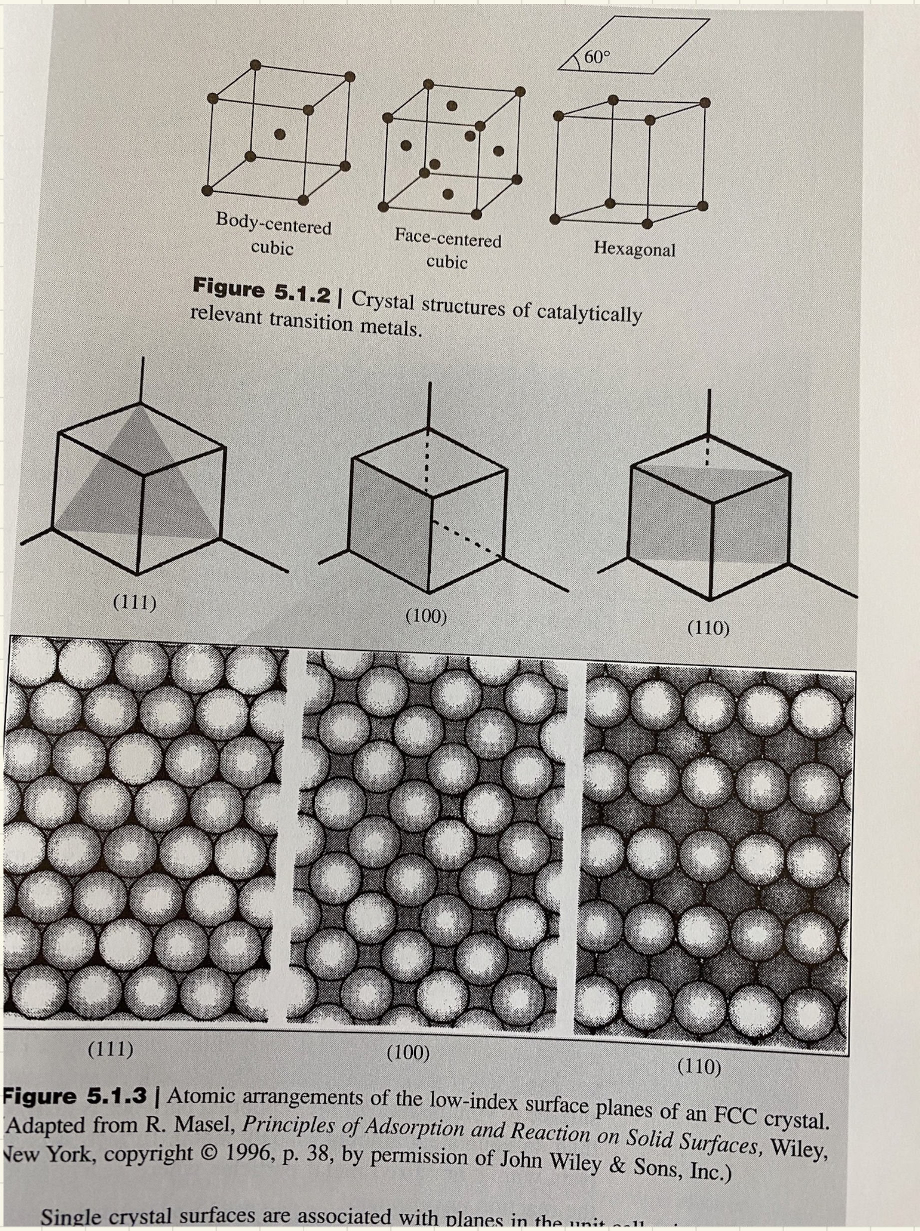


Figure 5.1.2 | Crystal structures of catalytically relevant transition metals.

Figure 5.1.3 | Atomic arrangements of the low-index surface planes of an FCC crystal. (Adapted from R. Masel, *Principles of Adsorption and Reaction on Solid Surfaces,* Wiley, New York, copyright © 1996, p. 38, by permission of John Wiley & Sons, Inc.)

Single crystal surfaces are associated with planes in the unit cell

EXACT SURFACE STRUCTURE MATTERS

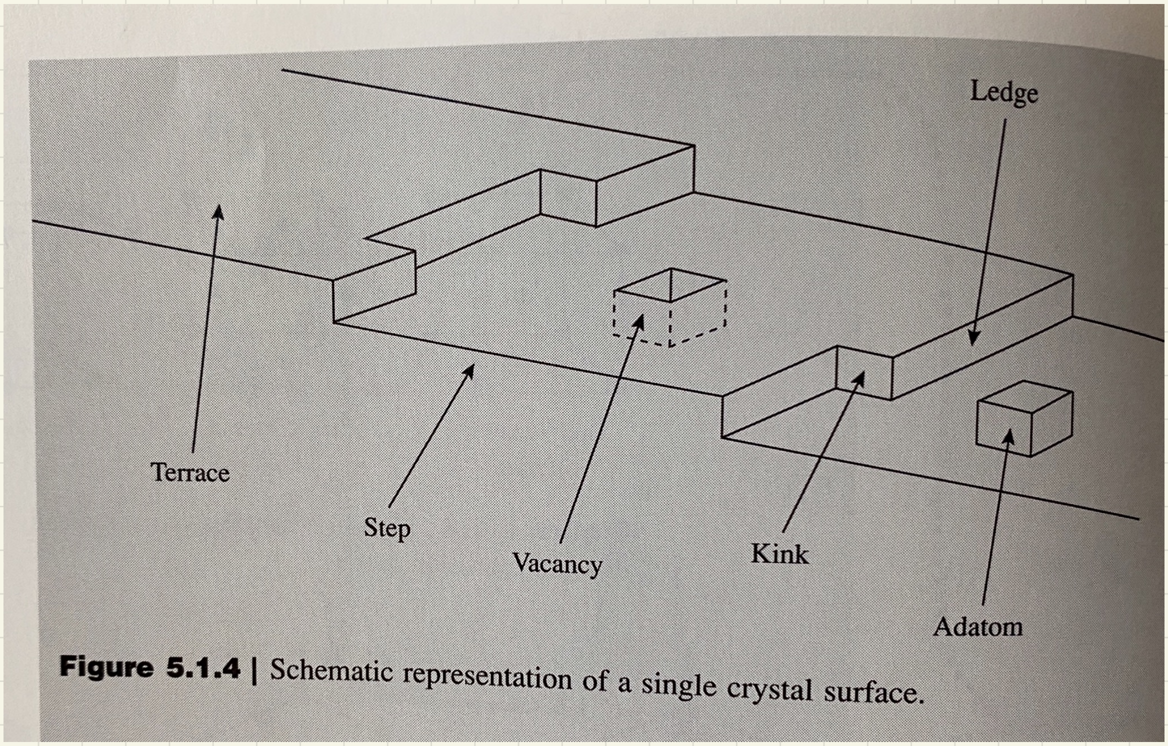


Figure 5.1.4 | Schematic representation of a single crystal surface.

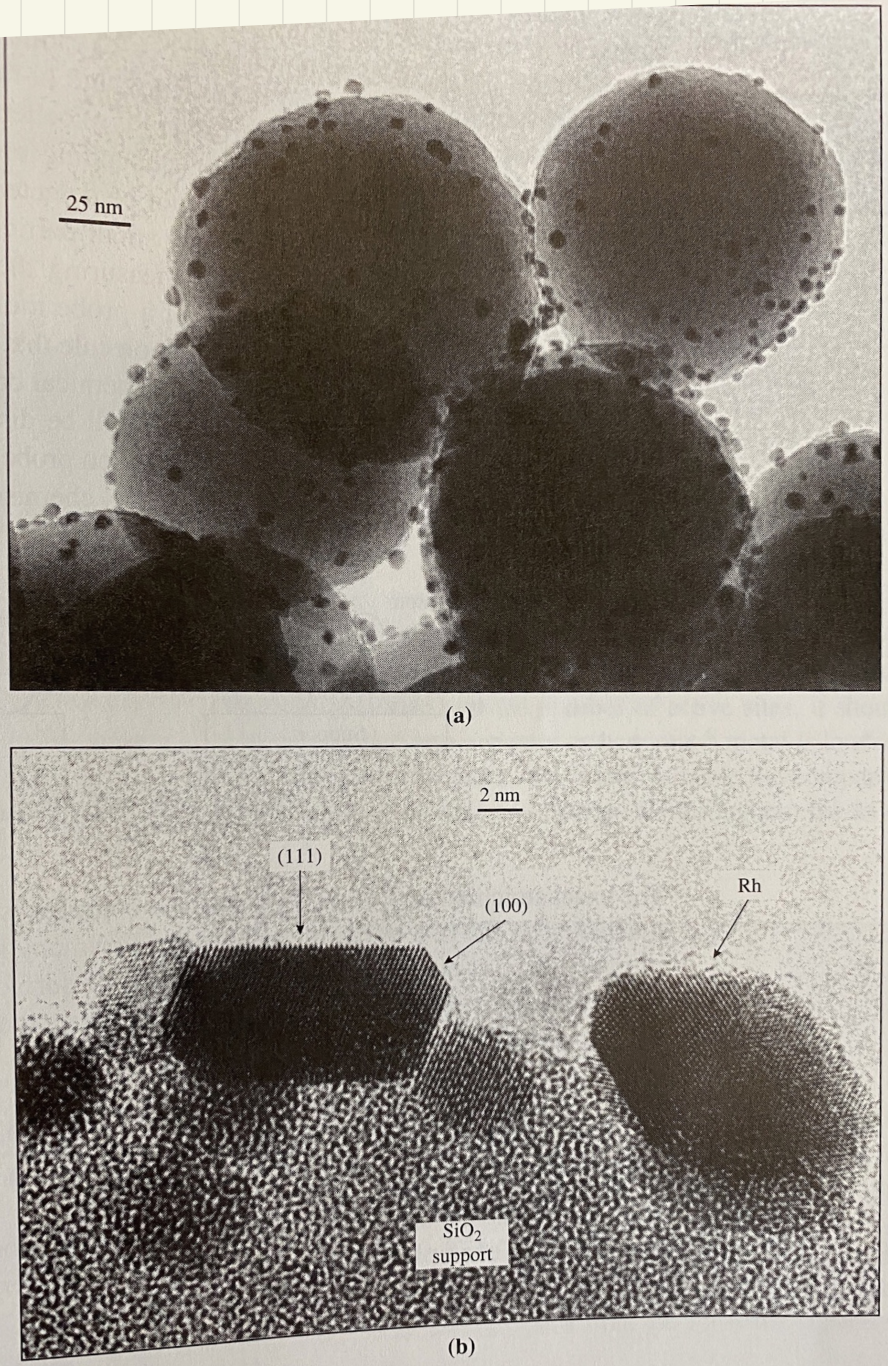


Figure 5.1.5 |
(a) Rhodium metal particles supported on silica carrier. (b) High-resolution electron micrograph shows how small supported Rh crystallites expose low-index faces. (Top photo courtesy of A. K. Datye. Bottom photo from "Modeling of heterogeneous catalysts using A. K. Datye in *Topics in Catalysis*, vol. 13:131,

IF WE CAN STUDY REACTIONS AT THIS SCALE, THE RATE CAN BE GIVEN AS

$$r_t = \frac{1}{S}\frac{dn}{dt}$$

NUMBER OF ACTIVE SITES.

TURNOVER FREQUENCY

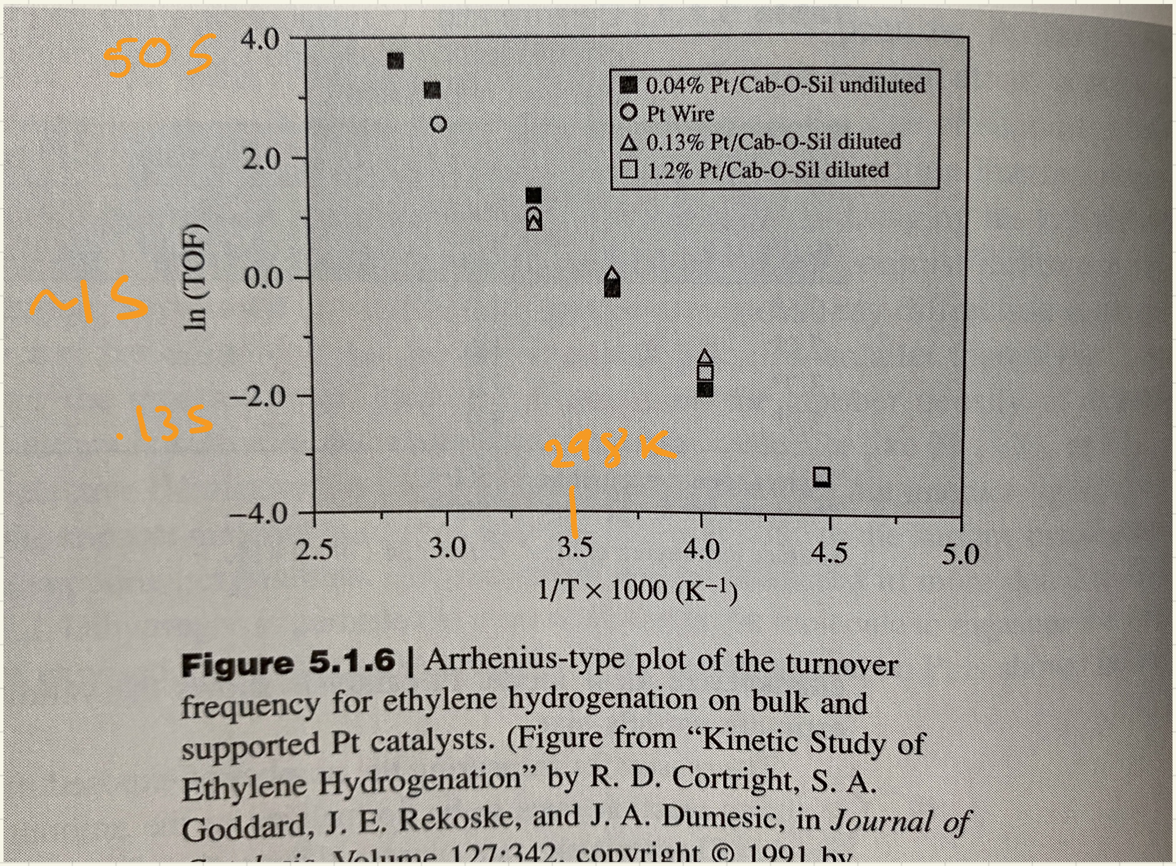


Figure 5.1.6 | Arrhenius-type plot of the turnover frequency for ethylene hydrogenation on bulk and supported Pt catalysts. (Figure from "Kinetic Study of Ethylene Hydrogenation" by R. D. Cortright, S. A. Goddard, J. E. Rekoske, and J. A. Dumesic, in *Journal of Catalysis*, Volume 127:342, copyright © 1991 by

THE CATALYST IS A SOLID SURFACE

THE REACTANT IS OFTEN A GAS, COULD BE A LIQUID IN A SOLVENT, BUT IN EITHER CASE A NECESSARY STEP IS ADSORPTION ONTO THE SURFACE

THE ADSORPTION PROBABLY HAS TO BE TO A SPECIFIC "SITE"

HENCE WE NEED NOTATION

" $\ast$ " ACTIVE SITE

$$A + \ast \underset{k_{DES}}{\overset{k_{ADS}}{\rightleftharpoons}} A\ast$$

ADSORPTION OF A GAS ONTO A SURFACE CAN BE

A) PHYSICAL ~ CONDENSATON ↑ ~ "PHYSISORPTION" ΔH

OCCURS "ANYWHERE" ON SOLID

B) CHEMICAL ~ ΔH_{Rxn}

"CHEMISORPTION"

OCCURS AT SPECIFIC SITES

SIMPLEST MODEL FOR ADSORPTION

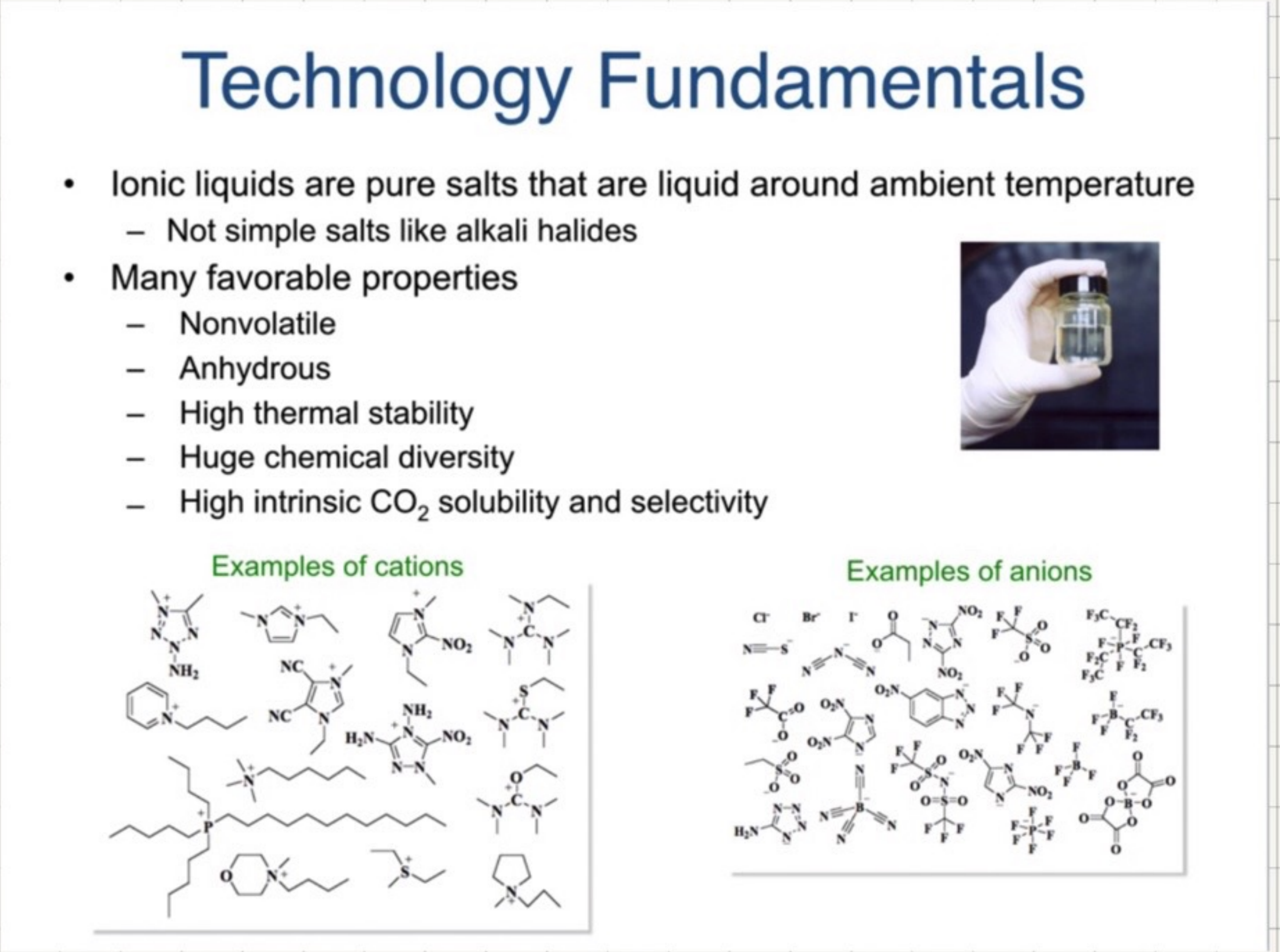
"LANGMUIR"

- PHYSICAL ADSORPTION OF
- 1 LAYER COVERAGE
- IDENTICAL SITES THAT DON'T INTERACT
- EQUILIBRIUM BETWEEN GAS PHASE AN CONDENSED COMPONENT ON SURFACE
- SHOWS HOW TEMPERATURE AFFECTS ADSORBED AMOUNT
- OFTEN WORKS WHEN YOU MIGHT NOT EXPECT....

BUT!!

- PERILS IN STRETCHING TOO FAR!!

WE HAVE FOUND THAT CHEMICAL COMPLEXATION OF GASEOUS CO_2 WITH 'DESIGNER' IONIC LIQUIDS FOLLOWS LANGMUIR

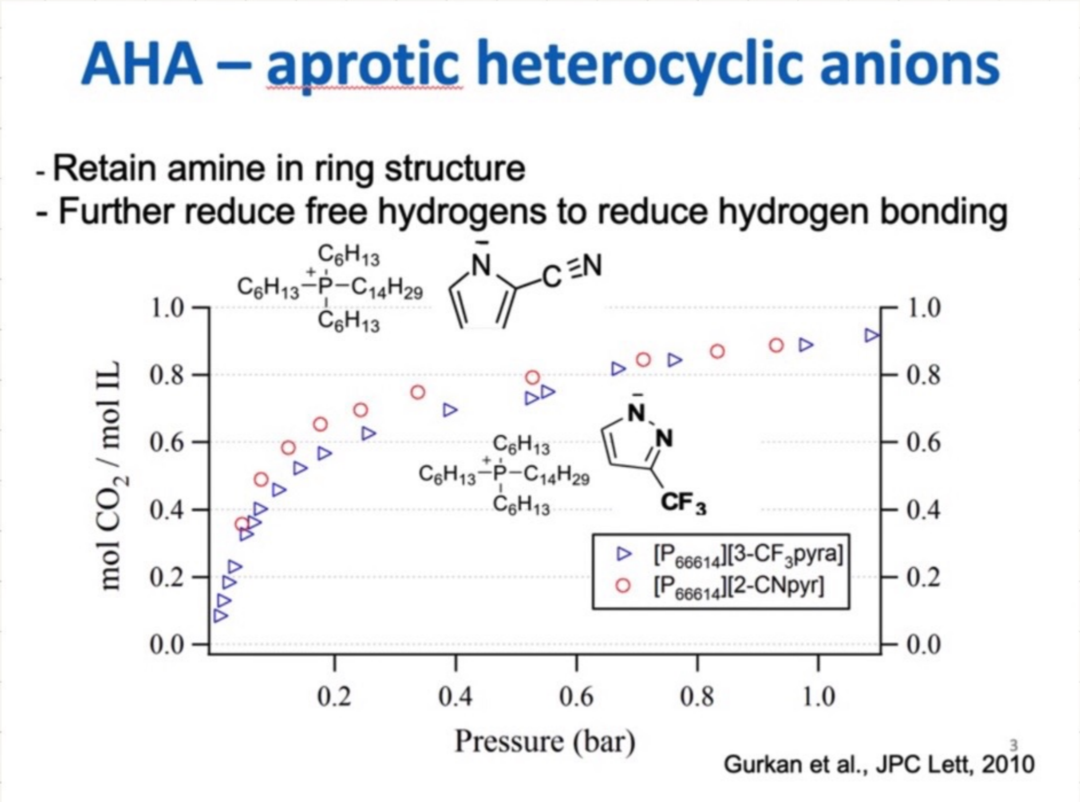


Technology Fundamentals

- Ionic liquids are pure salts that are liquid around ambient temperature
  - Not simple salts like alkali halides
- Many favorable properties
  - Nonvolatile
  - Anhydrous
  - High thermal stability
  - Huge chemical diversity
  - High intrinsic CO_2 solubility and selectivity

Examples of cations

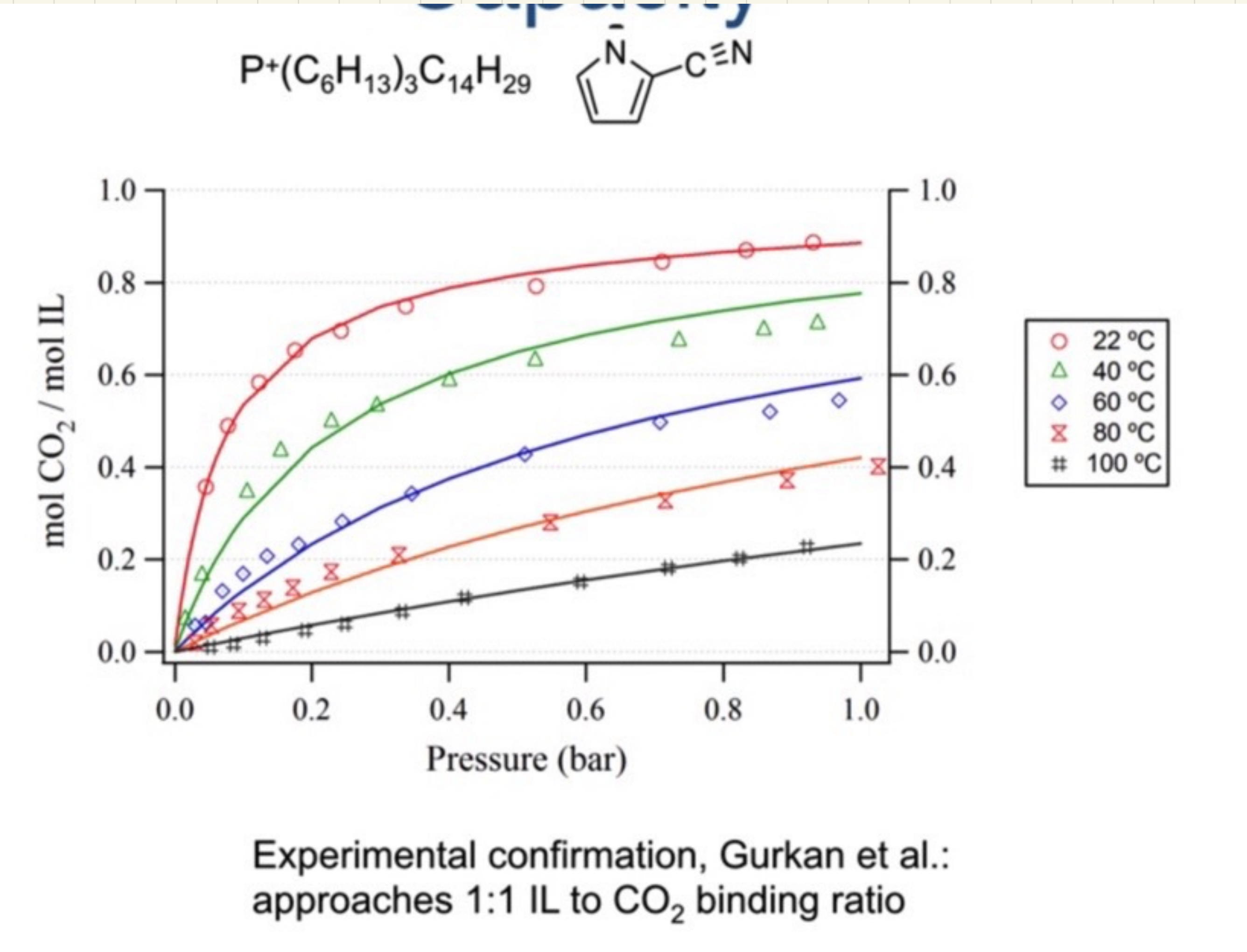
Examples of anions



AHA – aprotic heterocyclic anions

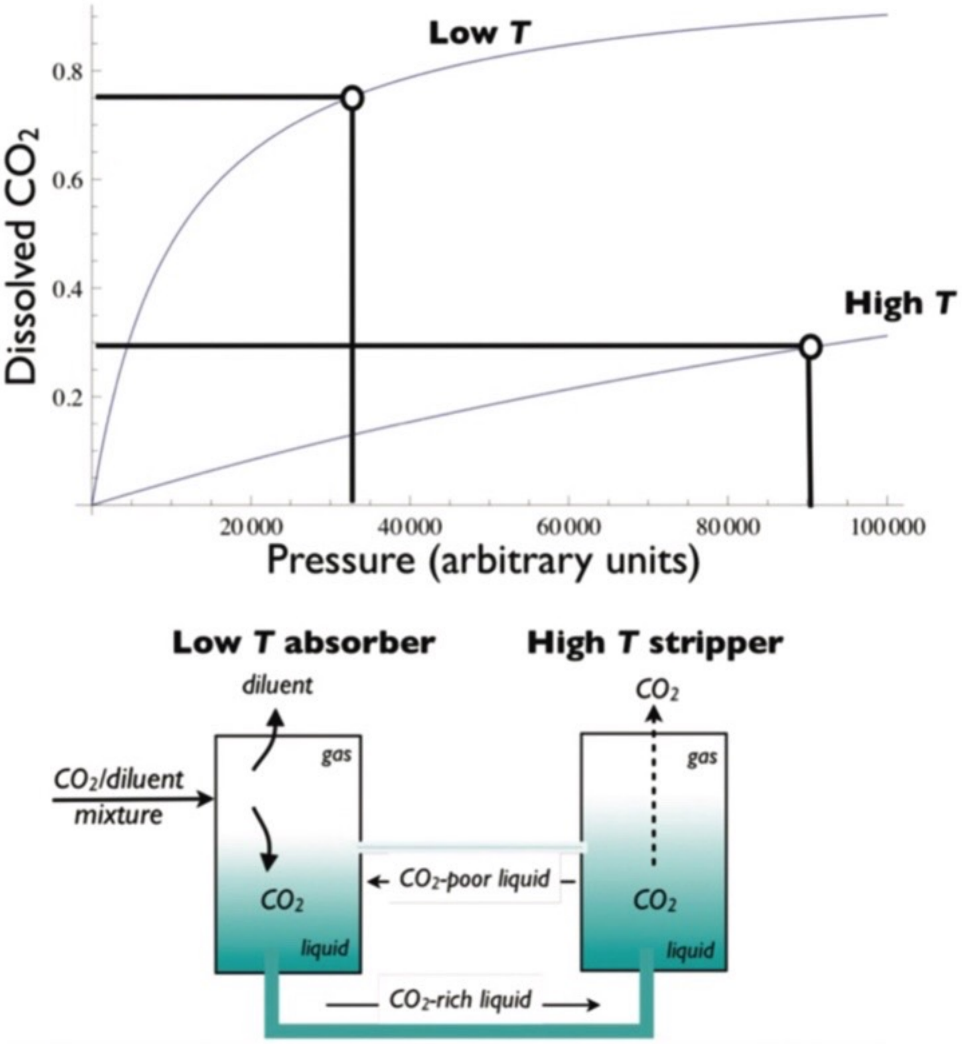
- Retain amine in ring structure
- Further reduce free hydrogens to reduce hydrogen bonding

Gurkan et al., JPC Lett, 2010

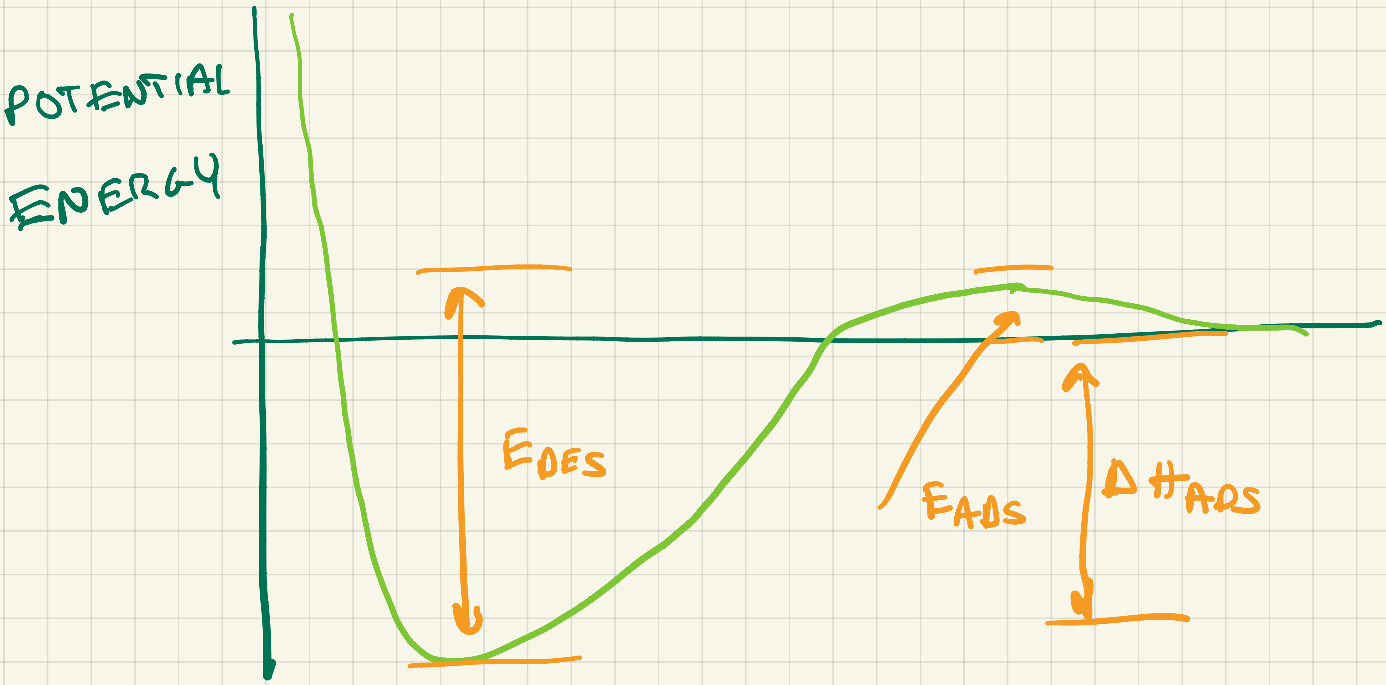


Experimental confirmation, Gurkan et al.:
approaches 1:1 IL to CO_2 binding ratio

THE JOURNAL OF PHYSICAL CHEMISTRY Letters



ENERGY DIAGRAM FOR ADSORPTION



THIS IS AN EQUILIBRIUM PROCESS BUT DERIVATION IS SIMPLEST IN TERMS OF RATES,

RATE OF ADSORPTION

=

RATE OF DESORPTION

$S = *$

GAS PRESSURE

$$r_{AD} = k_{AD} P_A [S]$$

CONCENTRATION OF SURFACE SITES

$$r_D = k_D [A_{AD}]$$

$$k_{AD} P_A [S] = k_D [A_{AD}]$$

RATE OF ADSORPTION = RATE OF DESORPTION

$$\frac{[A_{AD}]}{P_A [S]} = \frac{k_{AD}}{k_D} = K^A_{EQ}$$

TOTAL SITES

$$[S_0] = \frac{S_0}{a}$$

AREA

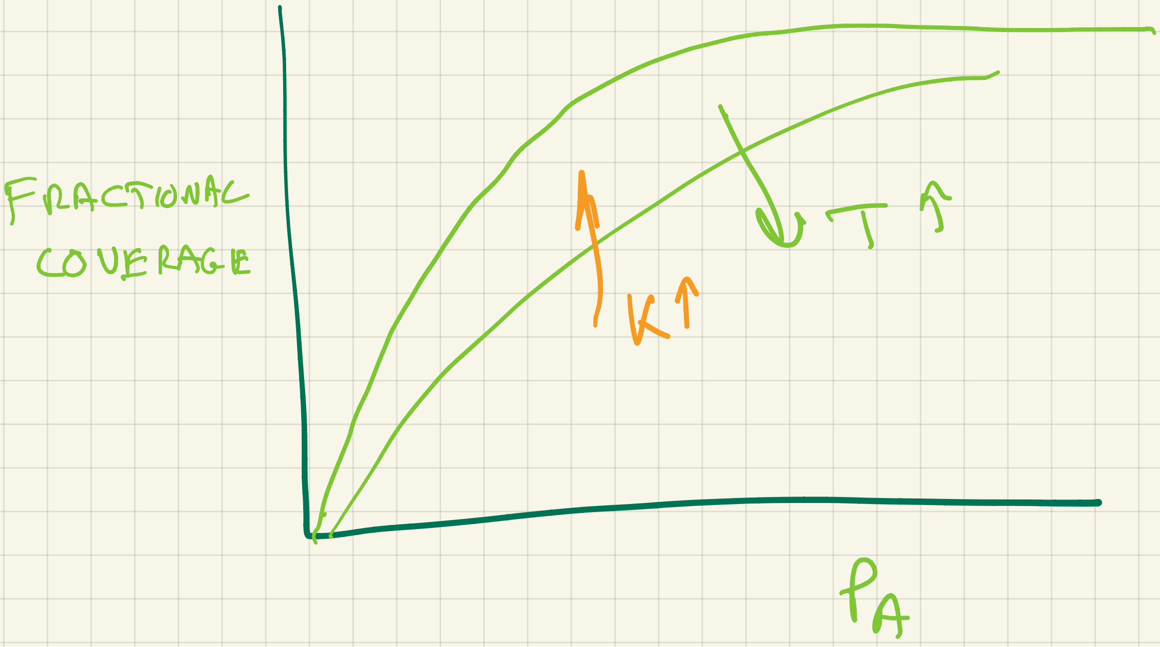
$$[S_0] = [S] + [A_{AD}]$$

$$[S_0] = \frac{[A_{AD}]}{K^A_{EQ} P_A} + [A_{AD}] = \frac{1 + K^A_{EQ} P_A}{K^A_{EQ} P_A} [A_{AD}]$$

$$\theta_A = \frac{[A_{AD}]}{[S_0]}$$

FRACTIONAL COVERAGE

$$\theta_A = \frac{K^A_{EQ} P_A}{1 + K^A_{EQ} P_A}$$



$$\Delta G = \underset{\substack{\uparrow \\ \text{NEGATIVE}}}{\Delta H} - T\underset{\substack{\uparrow \\ \text{MOST LIKELY NEGATIVE}}}{\Delta S}$$

MORE GENERAL ADSORPTION MODELS EXIST

B.E.T. BRUNAUER, EMMET, TELLER

MULTILAYER

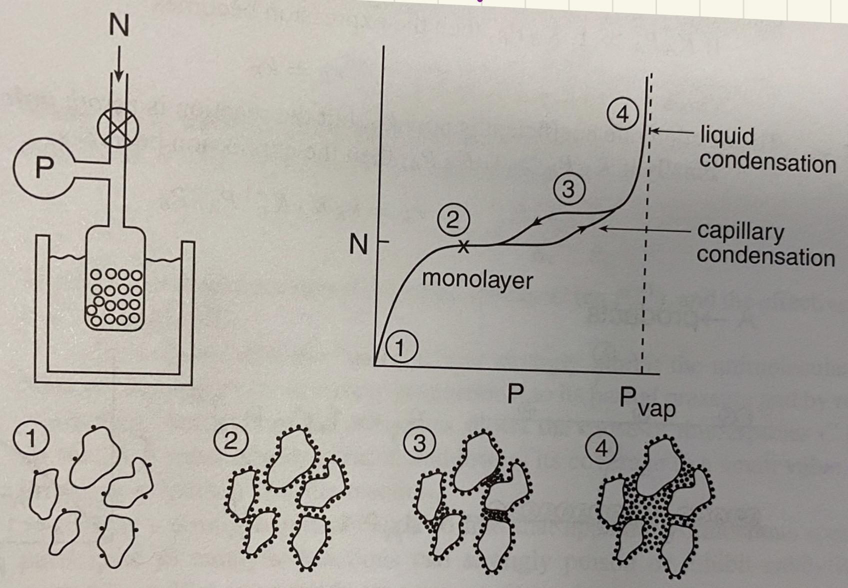


Figure 7–24 Adsorption equilibrium apparatus to determine adsorption isotherms and surface areas of catalysts. From the saturation of a sample of known weight, the surface area can be determined if the area occupied by a molecule is known. (Adsorbed molecules are dots.)

FROM L. SCHMIDT THE ENGINEERING OF CHEMICAL REACTIONS

$$\frac{P}{V_{ADS}(P_0-P)} = \frac{1}{cV_m} + \frac{c-1}{cV_m}\frac{P}{P_0}$$

GAS PRESSURE

SAT. PRESS

VOLUME OF GAS ADSORBED

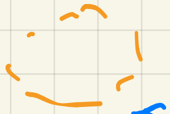
VOLUME OF GAS THAT GIVES A MONOLAYER

FITTED CONSTANT

GET c, V_m FROM FIT OF DATA

NUMBER OF MOLECULES

$N = 12$

$\alpha =$ 

$\frac{\text{AREA}}{\text{MOLECULE}}$

KNOWN VALUE

$$S_g = N \alpha$$

$$N = \frac{V_m N_0}{V}$$

STANDARD MOLAR VOLUME OF GAS

TYPICAL DERIVATION OF RATE EXPRESSION

$$A \longrightarrow M$$

① $A + * \xrightarrow[k_{des}]{k_{ads}} A^*$ ADSORPTION

② $A^* \xrightarrow{k_2} M + *$ SURFACE REACTION

THE RATE MUST BE: $r = k_2 [A^*]$

WE NEED TO GET A^* THUS
WE NEED $* + A^*$

$$[*]_0 = [A^*] + [*]$$

USE STEADY STATE!

$$\frac{dA^*}{dt} = 0 = k_{ads}[A][*] - k_{des}[A^*] - k_2[A^*]$$

$$[*]_0 = [A^*] + [*]$$

$$[*] = [*]_0 - [A^*]$$

$$\downarrow$$

$$0 = k_{ads}[A][*] - k_{des}[A^*] - k_2[A^*]$$

SOLVE FOR $[A^*]$

$$[A^*] = \frac{k_{ads}[A][*]_0}{k_2 + k_{ads}[A] + k_{des}}$$

$$= \frac{\frac{k_{ads}}{k_{des}}[A][*]_0}{1 + \frac{k_2}{k_{des}} + \frac{k_{ads}}{k_{des}}[A]}$$

$$\frac{k_{ads}}{k_{des}} = K_{ads}$$

$$\therefore \quad r = \frac{k_2 K_{ads}[A][*]_0}{1 + K_{ads}[A] + \frac{k_2}{k_{des}}}$$

CONSIDER A SLIGHTLY MORE COMPLEX CASE

$$A + B \longrightarrow M$$

EQ ADSORPTION $A + * \rightleftharpoons A^*$

EQ ADSORPTION $B + * \rightleftharpoons B^*$

SURFACE $A^* + B^* \xrightarrow{k_2} M + 2*$

RATE → $k_2 A^* B^*$

BUT FOR A SURFACE REACTION WE KNOW THAT EQ ASORPTION STEP GIVES A FRACTIONAL COVERAGE SO IT IS CONVENIENT TO WRITE:

$$\text{RATE} = k_3 [*]_0 \frac{A^*}{[*]_0} \frac{B^*}{[*]_0}$$

$$= k_3 [*]_0 \theta_A \theta_B$$

WHERE $k_3 = k_2 [*]_0$

AND $\theta_A = \dfrac{K_{adsA}[A]}{1 + K_{adsA}[A] + K_{adsB}[B]}$

$$\theta_B = \frac{K_{adsB}[B]}{1 + K_{adsA}[A] + K_{ads}[B]}$$

$$r = \frac{k_3 K_{adsA} K_{adsB} [*]_0 [A][B]}{\left(1 + K_{adsA}[A] + K_{adsB}[B]\right)^2}$$

2 *'S ARE INVOLVED