CBE 40445
9/18/20

HETEROGENEOUS CATALYSIS

→ KEY POINT IS THAT THE ADSORPTION OF A REACTANT OR REACTANTS ONTO SURFACE -- PERHAPS AT A SPECIFIC SITE -- IS CRUCIAL TO BOTH ENERGETICS + KINETICS OF A REACTION

THUS WE DESCRIBE LANGMUIR ADSORPTION

→ PHYSICAL PROCESS

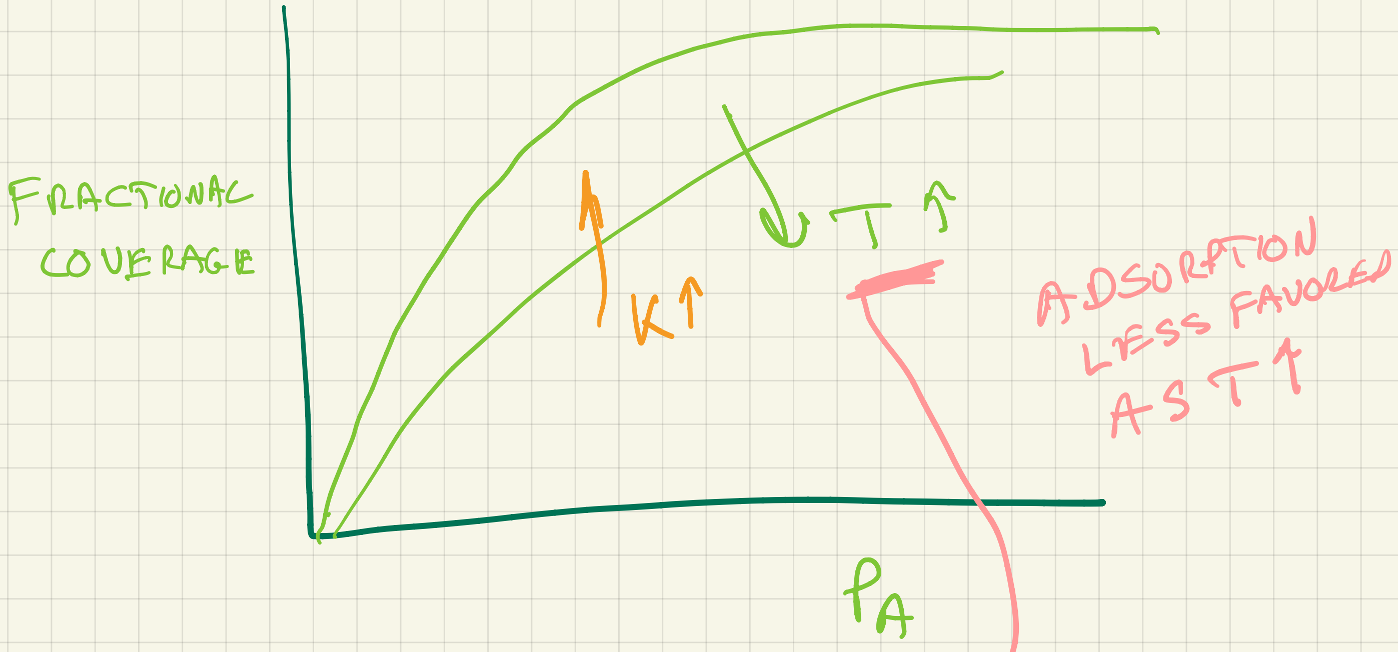
– SINGLE LAYER

TO DEMONSTRATE THIS EFFECT

$$A + * \underset{k_{des}}{\overset{k_{ads}}{\rightleftharpoons}} A^*$$

$$K_{ads} = \frac{k_{des}}{k_{ad}} = \frac{[A^*]}{[A][*]}$$

$$\theta_A = \frac{K_{ads}[A]}{1 + K_{ads}[A]}$$



$$\Delta G = \Delta H - T\Delta S$$

↑ NEGATIVE

↑ MOST LIKELY NEGATIVE

MORE GENERAL ADSORPTION MODELS EXIST

B.E.T. BRUNAUER, EMMET, TELLER

MULTI LAYER

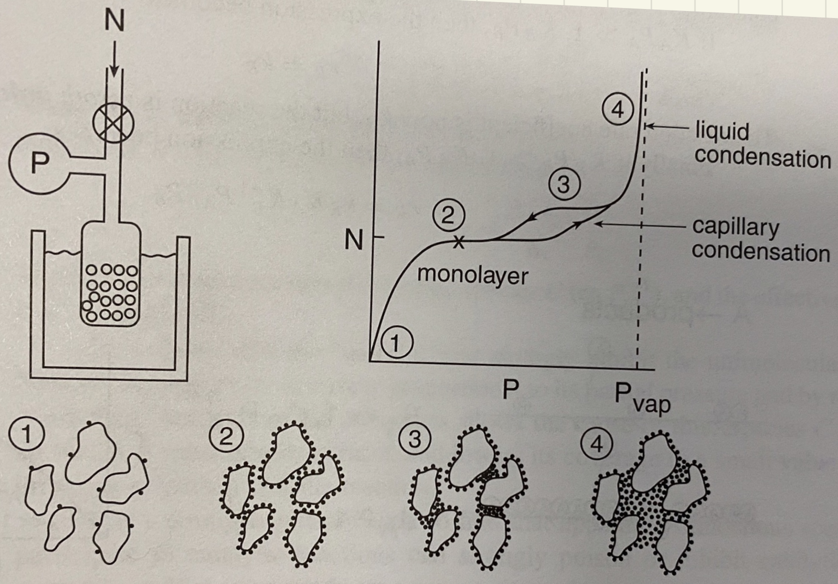


Figure 7–24 Adsorption equilibrium apparatus to determine adsorption isotherms and surface areas of catalysts. From the saturation of a sample of known weight, the surface area can be determined if the area occupied by a molecule is known. (Adsorbed molecules are dots.)

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

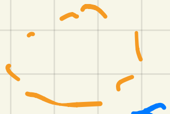
VOLUME OF GAS THAT GIVES A MONOLAYER

FITTED CONSTANT

GET c, V_m FROM FIT OF DATA

NUMBER OF MOLECULES

$N = 12$

$\alpha =$ 

AREA / MOLECULE

KNOWN VALUE

$$S_g = N \alpha$$

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

AVAGADRO'S #

STANDARD MOLAR VOLUME OF GAS

EVEN IF S_g IS NOT EXACTLY "CORRECT," IT IS OBTAINED BY A PRESCRIBED EXPERIMENT SO RESULT CAN BE REPLICATED & DIFFERENT CATALYSTS/SUPPORTS CAN BE COMPARED.

TYPICAL DERIVATION OF RATE EXPRESSION

$$A \longrightarrow M$$

① $A + * \underset{k_{des}}{\overset{k_{ads}}{\rightleftharpoons}} A^*$ ADSORPTION

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

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

SO WE WORK TO GET $[A^*]$

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

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

SITE BALANCE

USE STEADY STATE!

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

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

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

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

SOLVE FOR $[A^*]$

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

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

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

rate $= k_2[A^*]$

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

IF REACTION IS SLOW LAST TERM IS SMALL AND A ADSORPTION IS CLOSE TO EQUILIBRIUM

CONSIDER A SLIGHTLY MORE COMPLEX CASE

$$A + B \longrightarrow M$$

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

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

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

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 $k_3 = k_2 [*]_0$

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

LANGMUIR ADSORPTION

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

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

2 *'S ARE INVOLVED (

$$A + D \longrightarrow B$$

WITH INERT

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

EQ ADSORPTION $\quad D + * \rightleftharpoons D^*$

$$A^* + D^* \xrightarrow{k_2} B^*$$

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

EQ ADSORPTION $\quad I + * \rightleftharpoons I^*$

THUS: RATE → $k_2 A^* D^*$

ULTIMATELY, D^* WILL BE IN EXCESS

RESTRICT TO CASE WHERE REACTION IS SLOW, ALL ADSORPTION IS IN EQUILIBRIUM

FIRST LOOK AT ADSORPTION:

$$[*]_0 = [*] + [A^*] + [D^*] + [B^*] + [I^*]$$

$$[*]_0 = [*] + K_A[A][*] + K_D[D][*] + K_B[B][*] + K_I[I][*]$$

$$[*] = \frac{[*_0]}{1 + K_A[A] + K_D[D] + K_B[B] + K_I[I]}$$

NOW WE CAN GO TO RATE

$$r = k[A^*][D^*]$$

$$= k K_A[A][*] K_D[D][*]$$

NOW SUB IN FOR *

$$r = \frac{k K_A K_D [A][D][*]_0^2}{(1 + K_A[A] + K_D[D] + K_B[B] + K_I[I])^2}$$

NOW FOR CONST VOLUME DEVICE

$$[A] = \frac{\text{MOLES}}{V} = \frac{M_A}{V} = \frac{P_A}{RT}$$

$$r = \frac{k K_A' K_D' [*]_0^2 P_A P_D}{(1 + K_A' P_A + K_D' P_D + K_B' P_B + K_I' P_I)^2}$$

NOW IF $P_D >> P_A$, BUT $K_D' << K_A'$ ...

REACTION WILL BE PSEUDO FIRST ORDER

$$A \longrightarrow B$$

$$r \cong \frac{k'' K_A P_A}{(1 + K_A' P_A + K_B' P_B + K_I' P_I)^2}$$

https://www.youtube.com/watch?v=3ULzdD_0GXA

$$r = \frac{k' K_A' K_B' P_A P_B}{\left(1 + K_A' P_A + K_B' P_B + K_I' P_I\right)^2}$$

$$r = \frac{k'' K_A' P_A}{\left(1 + K_A' P_A + K_B' P_B + K_I' P_I\right)^2}$$

OK... SO ADSORPTION IS IMPORTANT.... CRITICAL, HOW DOES IT AFFECT ENERGETICS OF REACTION ?

HOW WILL AN ARRHENIUS PLOT LOOK ?

COMMON SITUATION

EX: $CO + {}^1/_2 O_2 \rightarrow CO_2$

1) $CO + * \overset{K_1}{\rightleftharpoons} CO^*$

$O_2 + * \xrightarrow{k_2} O*O$

$$r = 2k_2[O_2][*]$$

FOR HIGH SURFACE COVERAGE:

$$r = \frac{2k_2[*]_0[O_2]}{K_1[CO]}$$

APPARENT RATE CONST: $\frac{2k}{K_1}$

$$E_{App} = E_2 - \Delta H_{ads\ CO}$$

$+ \quad -(-) \quad = +$

THIS IS APPROXIMATELY

$$E_2 \widehat{=} -\Delta H_{ads\,CO}$$

SO WE SEE THAT E CAN BE STRONGLY INFLUENCED BY ΔH_{ads}

THIS SETS UP A COUNTER EXAMPLE

SIMPLE SURFACE CATALYZED REACTION $A \rightarrow M$

$$A + * \underset{k_{des}}{\overset{k_{ads}}{\rightleftharpoons}} A* \xrightarrow{k_2} M$$

$$r = \frac{k_2 K_{ads} [*]_* [A]}{1 + K_{ads}[A]} \qquad (5.2.22)$$

~EQUILIBRATED

IN LIMIT SUCH THAT SURFACE COVERAGE IS SMALL

$$r = k_2 K_{ads} [*]_0 [A]$$

WHICH GIVES $k_2 K_{ads}$ AS THE RATE CONSTANT:

$$\underset{(+)}{E_{app} = E_2} + \underset{(-)}{\Delta H_{ads}}$$

THE APPARENT ACTIVATION ENERGY CAN BE EITHER POSITIVE OR NEGATIVE !!

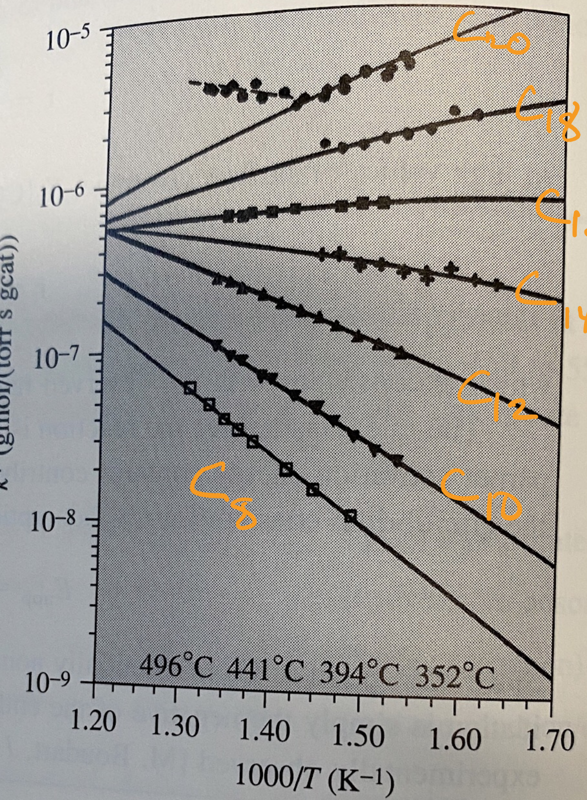


Figure 5.3.1 |
Temperature dependence of the cracking of n-alkanes. [Reprinted from J. Wei, "Adsorption and Cracking of N-Alkanes over ZSM-5: Negative Activation Energy of Reaction," *Chem. Eng. Sci.*, **51** (1996) 2995, with permission from Elsevier Science.] Open square—C_8, inverted triangle—C_{10}, triangle—C_{12}, plus—C_{14}, filled square—C_{16}, diamond—C_{18}, circle—C_{20}.

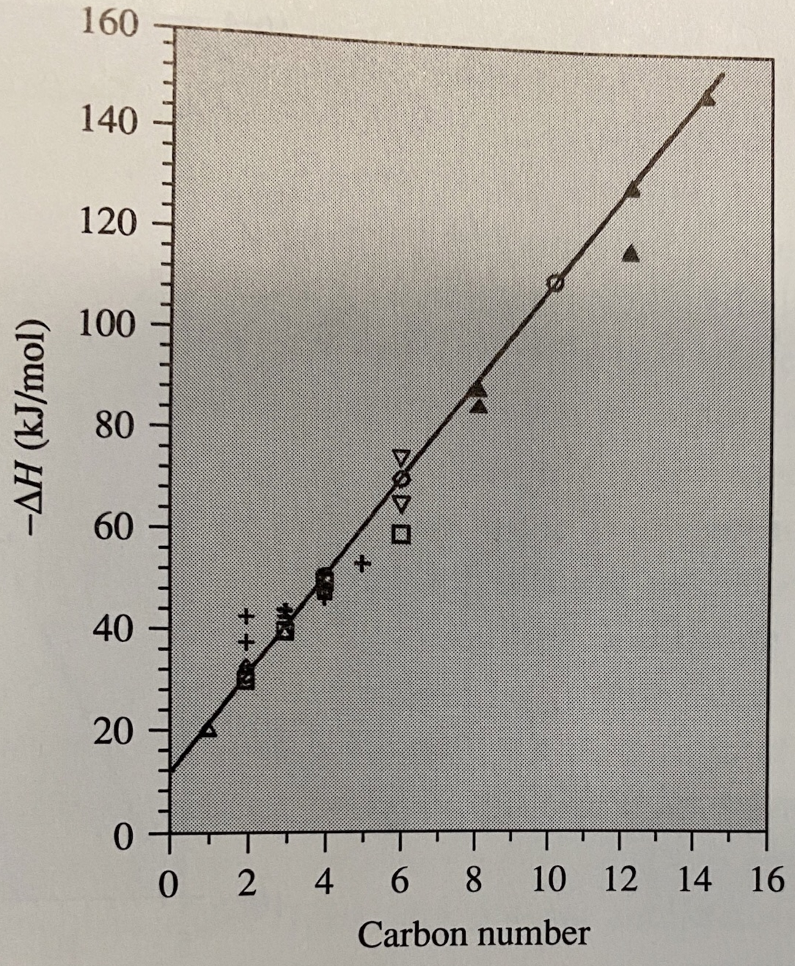


Figure 5.3.2 | Heats of adsorption of n-alkanes on ZSM-5. [Reprinted from J. Wei, "Adsorption and Cracking of N-Alkanes over ZSM-5: Negative Activation Energy of Reaction," *Chem. Eng. Sci.*, **51** (1996) 2995, with permission from Elsevier Science.]

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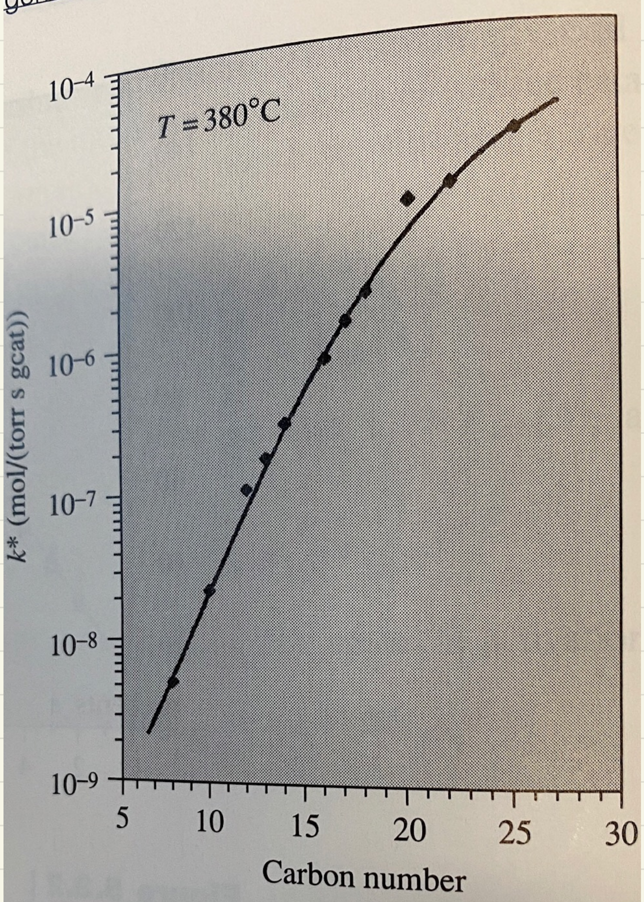


Figure 5.3.3 | The apparent first-order rate constant of n-alkane cracking over ZSM-5 at 380°C. [Reprinted from J. Wei, "Adsorption and Cracking of N-Alkanes over ZSM-5: Negative Activation Energy of Reaction," *Chem. Eng. Sci.*, **51** (1996) 2995, with permission from Elsevier Science.]

ZEOLITES

USED FOR CATALYSIS
AND ADSORPTION

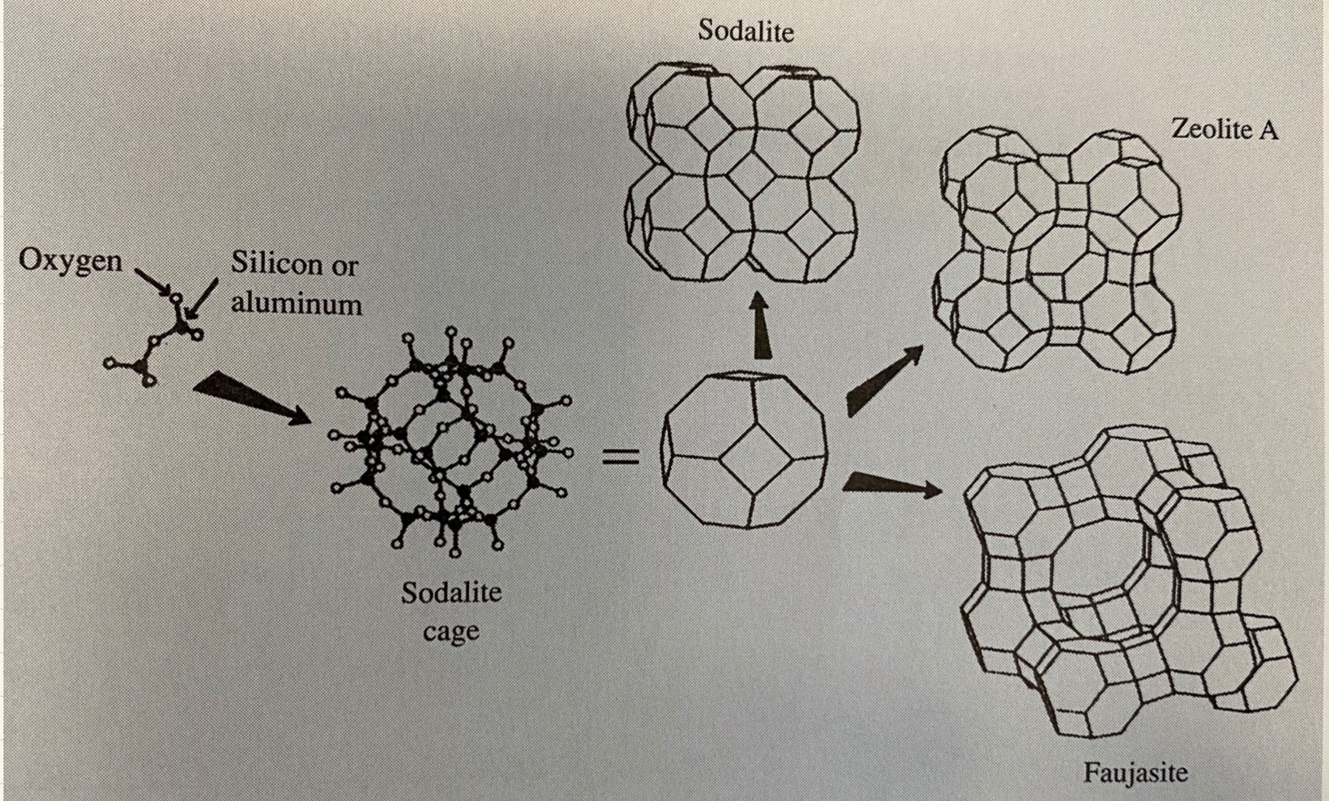


Figure 5.3.4 | Schematic of zeolite frameworks. The synthetic faujasites are NaX and NaY (difference between NaX and NaY is the ratio of Si to Al: NaX ~ 1.1, NaY ~ 2.4). These constructions do not represent how the materials are synthesized but rather their structural features alone. [Reprinted with permission from M. E. Davis, *Ind. Eng. Chem. Res.*, **30** (1991) 1676. Copyright 1991 American Chemical Society.]

M. DAVIS CONTRIBUTION

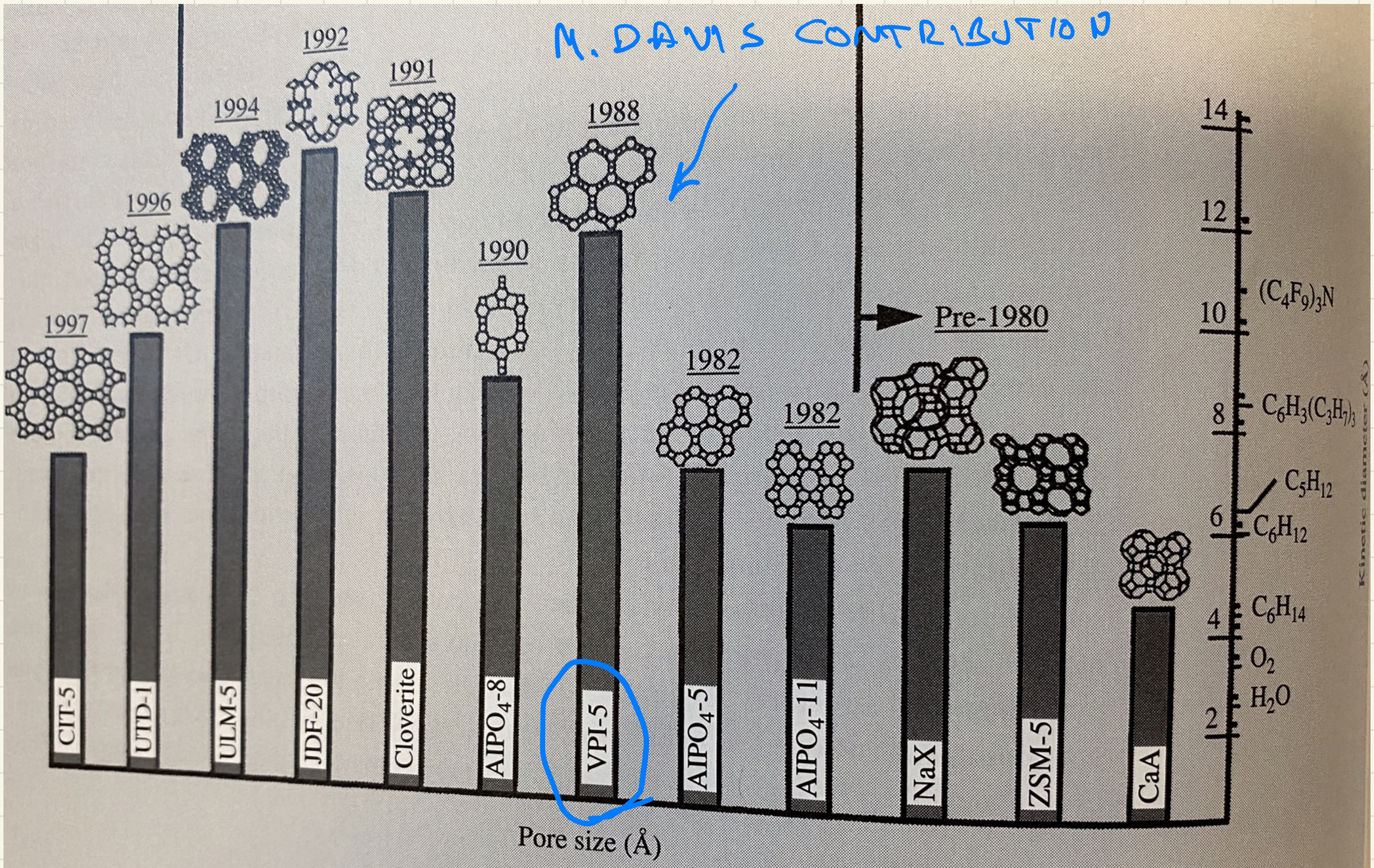


Figure 5.3.5 | Correlation between pore size of molecular sieves and the diameter of various molecules. [Reprinted from M. E. Davis, "Zeolite-Based Catalysts for Chemicals Synthesis," *Microporous and Mesoporous Mater.*, **21** (1998) 179, with permission of Elsevier Science.]

PRECISE PORE SIZE GIVES BEST POSSIBLE SELECTIVITY

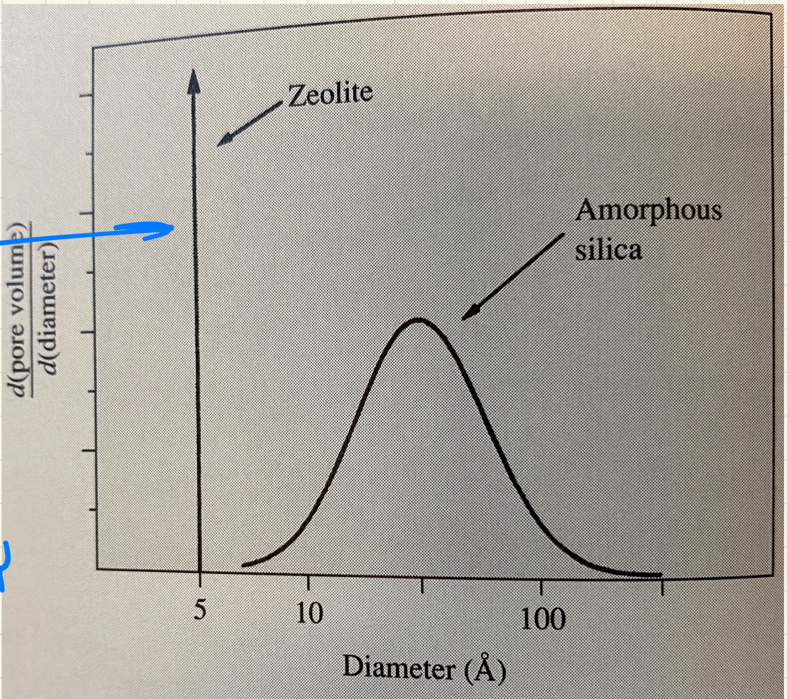


Figure 5.3.6 | Pore size distribution of zeolite compared to amorphous silica. [Reprinted with permission from M. E. Davis, *Ind. Eng. Chem. Res.*, **30** (1991) 1677. Copyright 1991 American Chemical Society.]

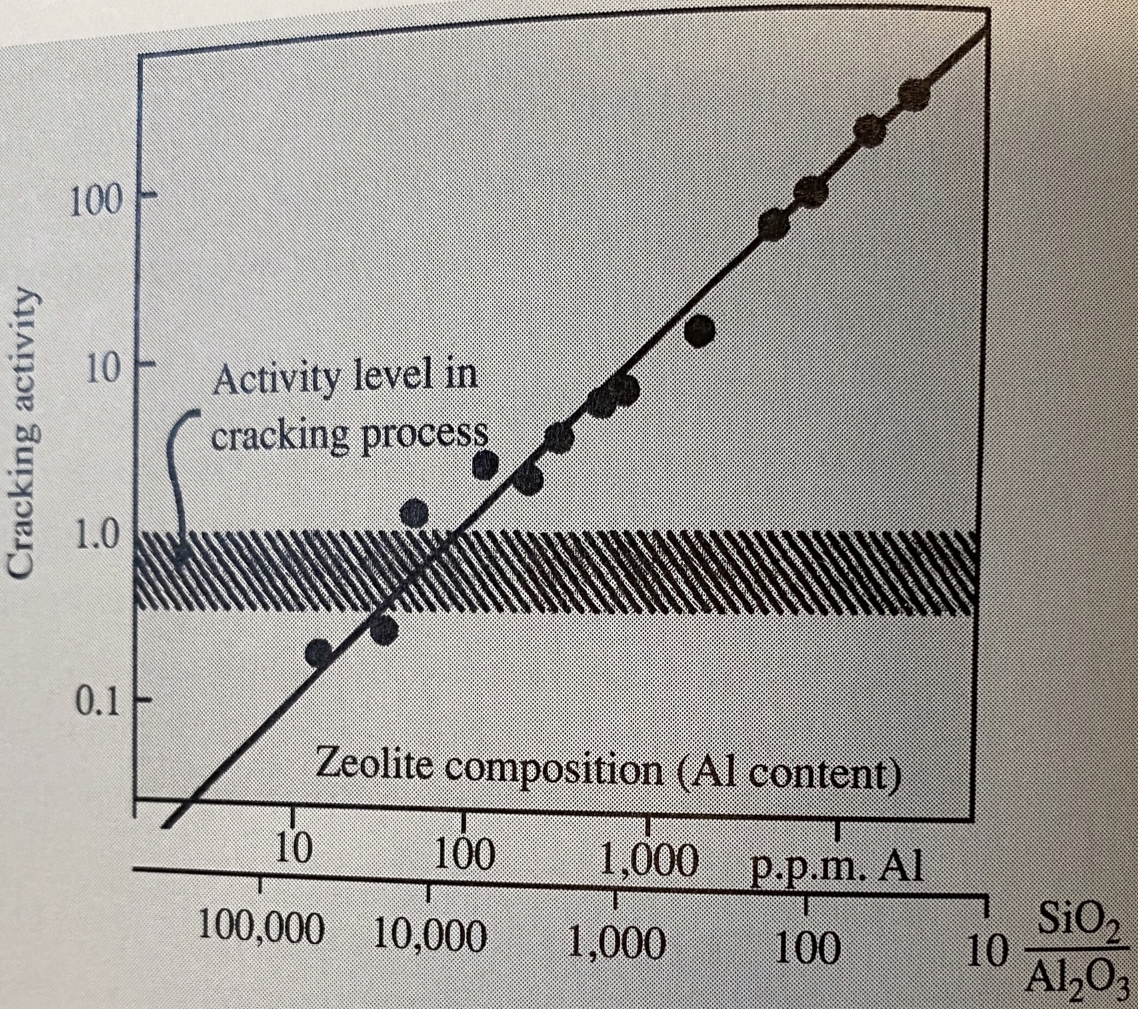
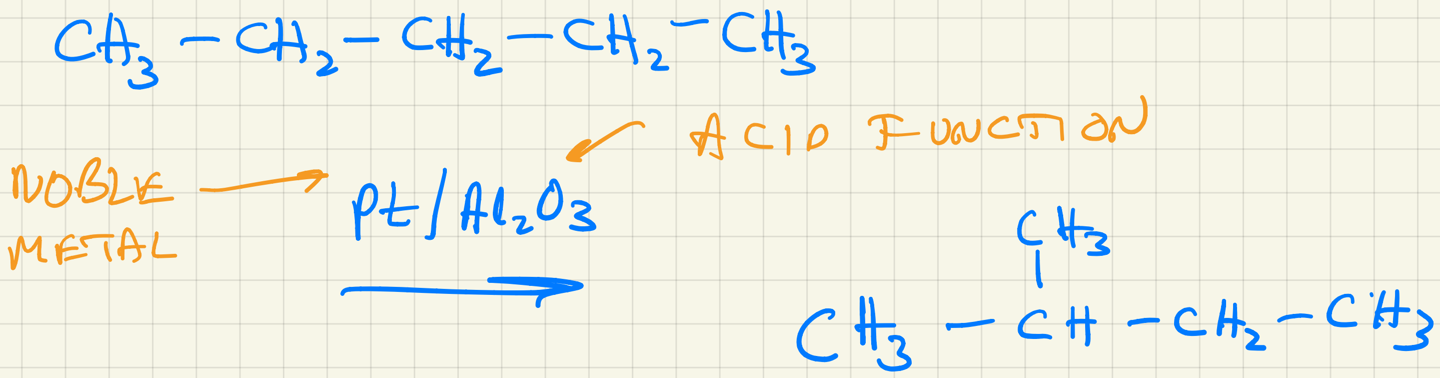


Figure 5.3.8 | Variation in the hexane cracking activity with aluminum content in ZSM-5. [Reprinted with permission from W. O. Haag, R. M. Lago, and P. B. Weisz, *Nature*, **309** (1984) 589.]

MULTIFUNCTIONAL CATALYSTS

REFORMING:



$$CH_3-CH_2-CH_2-CH_2-CH_3 \xrightarrow{Pt/Al_2O_3} CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_3$$

Pt CATALYZES HYDROGENATION/ DEHYDROGENATION

ACIDIC FUNCTION FACILITATES SKELETAL ISOMERIZATION

(END OF CHAPTER 5)