understanding chemistry by understanding photocatalysis
understanding photocatalysis by understanding chemistry

Division of Environmental Material Science, Graduate School of Environmental Science
The first semester of Fiscal 2017
08:45—10:15, Thursday at Lecture Room D103

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principle of photocatalytic reaction

electronic structure of semiconductors and insulators
conduction & valence bands separated by bandgap
photoexcitation beyond the bandgap

1. photoexcitation
2. electron and hole
3. relaxation
4. reduction & oxidation
5. recombination

ONLY thermodynamic aspects
NOT kinetic aspects

2017/05/18—Advanced Course in Environmental Catalytic Chemistry I
thermodynamics and kinetics

thermodynamics = equilibrium:
- considering the (chemical) energies of SOURCE and PRODUCT(S)
  without any information on the mechanism

kinetics:
- velocity of reaction to reach an equilibrium

Show $\Delta G$ and $E_a$ in this illustration
Honda-Fujishima effect: splitting of water

Photoirradiation of a titania electrode short-circuited with a platinum counter electrode DOES NOT induce splitting of water into hydrogen and oxygen

1) Application of bias potential which does not induce electrolysis of water in the dark
2) Use of higher and lower pH electrolytes for titania and platinum electrodes, respectively, i.e., chemical bias

Fig. 2. Electrochemical cell in which the TiO₂ electrode is connected with a platinum electrode (see text). The surface area of the platinum black electrode used was approximately 30 cm².
absorption edge wavelength

absorption edge: corresponding to band gap
apparently the edge is not SHARP due to distribution of "density of states"

DOS in the bands are not homogeneously distributed

negligible DOS at the edges = less photoabsorption

DOS
Density Of States
Localized/delocalized

Band model tells photoexcitation of electron in VB to CB. "delocalized" electrons and positive holes
How electrons and positive holes migrate in a photocatalyst?

cf. organic molecules
hypothesis for excitation to give electron-hole pairs

- Electron traps, i.e., vacant electronic level just below the CB bottom
- Excitation of electron in VB to CB occurs non-localized fashion.
- Non-localized electron in CB is localized at an electron trap without migration, i.e., just after excitation.
- Assuming higher density of electron traps on particle SURFACES,
  - Electrostatic interaction of electron and hole
  - Traps for positive hole may be present.
  - What is the SURFACE traps? Possible structure of anatase titania may be an adsorbed $O_2$. 
relaxation and recombination

femtosecond pump-probe photoabsorption spectroscopy

relaxation < 1 ps

-> pump-probe
electron-hole and relaxation

- photoexcitation: excited electron (e\textsuperscript{-}) in a conduction band (CB) and positive hole (h\textsuperscript{+}) in a valence band (VB)
- relaxation: e\textsuperscript{-} at the bottom of CB and h\textsuperscript{+} at the top of VB
- levels of energy of relaxed e\textsuperscript{-} and h\textsuperscript{+} not depending on the irradiation wavelength
photocatalytic reaction known in old times

- photoadsorption/desorption of oxygen
- chalking (not "choking")

**Diagram:**
- Titania particles
- Binder (organic compounds)
- Photocatalytic reaction
photocatalytic air purifier unit

active air purification:
decontamination and deodorization of circulating air

Hitachi Home and Life Solution
http://www.hitachi-hl.com/

Daikin Ltd.
http://www.daikinaircon.com/

air conditioner

air purifier
Pavements containing titania photocatalyst

"Photoroad"

Nitrogen oxides ($\text{NO}_x$) are oxidized by photocatalyst.
Resulting nitrate ($\text{NO}_3^-$) ions are captured by calcium ions.
Calcium nitrate ($\text{Ca(NO}_3\text{)}_2$) is washed out by rain water.
photocatalytic reaction

- photoabsorption to yield photoexcited electron ($e^-$) and positive hole ($h^+$)
- reaction of SURFACE-ADSORBED compounds with $e^-$ and $h^+$.
- In other words, only adsorbed compounds can be reacted.
adsorption isotherm

interaction of compounds with surfaces
• van der Waals force: physical adsorption
• chemical bond: chemisorption

concentration (pressure) dependence of adsorbed amount: isotherm
Q Answer the names of these isotherms.
three assumptions for derivation of Langmuir eq.

- 
- 
-
three assumptions for derivation of Langmuir eq.

- All the adsorption sites are same in quality, i.e., strength of capturing an adsorbate is constant.

- Only one adsorbate is adsorbed by one site.

- There is no interaction between sites, i.e., adsorption not influenced by adsorption of neighboring sites.
adsorption equilibrium

adsorption equilibrium:

same rates of adsorption and desorption

Adsorption rate depends on (1) concentration in bulk and (2) number (density) of vacant sites (V)

Desorption rate depends on number (density) of occupied sites (O).
rate \( (r) \) of reaction for

\[ A \rightarrow B \]

is expressed using \( k \) (rate constant) and concentrations of A and B \( ([A] \) and \( [B] \), respectively, as

\[ r_f = k_f [A] \]
\[ r_b = k_b [B] \]

For equilibrium, \( r_f = r_b \), then

\[ K = \frac{k_f}{k_b} = \frac{[B]}{[A]} \]
Q: Derive the Langmuir isotherm.

Same rate of adsorption and desorption at equilibrium
rate of adsorption: \( r_a = k_a[\nu]C \)
rate of desorption: \( r_d = k_d[\sigma] \)

\[
k_a[\nu]C = k_d[\sigma]
\]

\[
k_a C \frac{[\nu]}{([\nu]+[\sigma])} = k_d[\sigma]/([\nu]+[\sigma])
\]

\[
k_a C (1 - \theta) = k_d \theta
\]

\[
KC (1 - \theta) = \theta
\]

\[
\theta = \frac{KC}{1 + KC}
\]

vacant site: \([\nu]\), occupied site: \([\sigma]\), coverage \(\theta = \frac{[\sigma]}{([\nu] + [\sigma])}\), concentration at equilibrium: \(C\), rate constants: \(k_a\) and \(k_d\), adsorption equilibrium constant: \(K = \frac{k_a}{k_d}\)
adsorption and photocatalytic activity

- The larger the adsorbed substrate(s), the higher the activity.
- The larger the surface area, the larger the adsorbed amount.

Example

two limits for Langmuir isotherm

relation between actual adsorption amount and \( \theta \): saturation amount \( s \)

\[
[S]_{\text{ads}} = s \theta = \frac{sKC}{1 + KC}
\]

two limits

• When \( C \) is so small that \( KC \) can be neglected: \( [S]_{\text{ads}} \propto \)

• When \( C \) is large enough to neglect "1": \( [S]_{\text{ads}} = \)}
two limits for Langmuir isotherm

relation between actual adsorption amount and $\theta$: saturation amount $s$

$$[S]_{\text{ads}} = s\theta = \frac{sKC}{1 + KC}$$

two limits

• When $C$ is so small that $KC$ can be neglected: $[S]_{\text{ads}} \propto C$

• When $C$ is large enough to neglect "1": $[S]_{\text{ads}} = s$
Langmuir isotherm

There are two limits: linear part and saturated part.

\[
[S]_{ads} = s \theta = \frac{sKC}{1 + KC}
\]
Q Answer the names of these isotherms.

- Henry
- Langmuir
- BET
- Freundlich
Q: Who are BET?

\[ \nu = \frac{\nu_m c \chi}{(1-x)(1-x + c \chi)} \]

\( \nu_m \): saturation amount of first layer of adsorption

\( c \): a constant

\( x \): relative pressure (0-1)
Brunauer–Emmett–Teller isotherm

\[ v = \frac{v_m cx}{(1-x)(1-x+cx)} \]

- \( v_m \): saturation amount of first layer of adsorption
- \( c \): a constant
- \( x \): relative pressure (0-1)

*a kind of "agglomeration"*

\[ \frac{x}{v(1-x)} = \frac{1}{v_m c} + \frac{c-1}{v_m c} x \]

得られた1層めの飽和吸着量に窒素の吸着断面積(0.162 nm²)をかけて表面積(m²)をとめ、さらにつかった固体量でわって比表面積(m² g⁻¹)とする。
Q: How is relative pressure, $x$, measured?

$$v = \frac{v_m c x}{(1-x)(1-x+cx)}$$

$v_m$: saturation amount of first layer of adsorption
$c$: a constant
$x$: relative pressure (0-1)

$x$: pressure of nitrogen measured under the same CONDITIONS = saturated vapor pressure of nitrogen

The condition: boiling point of nitrogen at the temperature of liquid nitrogen in a Dewar bottle, and the vapor pressure is the same at atmospheric pressure around an instrument. Therefore, atmospheric pressure has to be measured.
If a compound adsorbed on a photocatalyst surface in Langmuirian fashion is oxidized (or reduced) by the positive hole (or photoexcited electron) in the photoirradiated photocatalyst, what is a rate expression for the reaction?
Please send email in Japanese or English within 48 hours

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pc20170518-XXXXXXXX
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大谷文章
某教授
光触媒の応用例について知り、その基本が化学であることを学びました。光と物質のかかわりについてさらに知りたいので本を調べてみます。
絶版になっている「光触媒標準研究法」はどこかで入手可能ですか。