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 2014
08:45—10:15, Thursday at Lecture Room D103

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<< objectives >>
Understanding the mechanism of decomposition of pollutants, methods of photocatalysts preparation, design of practical photocatalytic reaction systems, and strategy for enhancement of photocatalytic activity.

<< goal >>
To understand principle of photocatalytic reaction from the standpoint of chemistry and strategy for practical applications. To obtain scientific method for research on functional solid materials.

<< keywords >>
Photocatalyst, Photoinduced oxidative decomposition, Superhydrophilicity, Excited electron-positive hole, Structure-activity correlation, Higher photocatalytic activity, Visible-light response
schedule

(1) April 10 introduction of photocatalysis
(2) April 17 interaction between substances and light
(3) April 24 electronic structure and photoabsorption
(4) May 1 thermodynamics: electron and positive hole
(5) May 8 adsorption
(6) May 15 (Professor Ewa Kowalska)
(7) May 22 kinetic analysis of photocatalysis
(8) May 29 steady-state approximation
(9) June 5 kinetics and photocatalytic activity
(10) June 12 kinetic analysis
(11) June 19 (Professor Mai Takase)
(12) June 26 action spectrum analysis (1)
(13) July 3 action spectrum analysis (2)
(14) July 10 crystal structure of titania
(15) July 17 design and development of photocatalysts
  July 24 deadline for submission of special report
comments on this lecture

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(full name)
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(comments and/or questions on today's lecture)
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
Answer the names of these isotherms.

- **A** Henry
- **B** Langmuir
- **C** Brunauer–Emmett–Teller
- **D** Freundlich
Q List up the three assumptions for Langmuir adsorption isotherm.
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.
Q: Derive the Langmuir isotherm.

Same rate of adsorption and desorption at equilibrium

rate of adsorption: \( r_a = k_a[v]C \)
rate of desorption: \( r_d = k_d[o] \)

\[
k_a[v]C = k_d[o]
\]
\[
k_aC \frac{[v]}{([v]+[o])} = k_d[o]/([v]+[o])
\]
\[
k_aC (1 - \theta) = k_d \theta
\]
\[
KC (1 - \theta) = \theta
\]

\[
\theta = KC/(1 + KC)
\]

vacant site: \([v]\), occupied site: \([o]\), coverage \(\theta = [o]/([v] + [o])\), concentration at equilibrium: \(C\), rate constants: \(k_a\) and \(k_d\), adsorption equilibrium constant: \(K = k_a/k_d\)
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).
Q How does Langmuirian equation show the characteristics of surface phenomenon?

\[ A + B \leftrightarrow A-B \]
rate ($r$) of reaction for

$$A \rightarrow B$$

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

$$r = k [A]$$
Why the rate is proportional to concentration?

Q Interpreted the reason why the rate is proportional to concentration?
kinetic energy = temperature (heat)

Translational motion: Average velocity is defined as "temperature". The higher the temperature, the more the number of particles (molecules) of higher kinetic energy.
 activation energy

- Arrhenius equation shows the relation between a rate constant ($k$) and activation energy ($E_a$) and temperature ($T$), as well as a constant $A$.

Q Show Arrhenius equation.
activation energy

- Arrhenius equation shows the relation between a rate constant \(k\) and activation energy \(E_a\) [J mol\(^{-1}\)] and temperature \(T/K\), using gas constant \(R\) and a constant \(A\).

- Arrhenius equation is

\[
k = A \exp\left(-\frac{E_a}{RT}\right).
\]

- This equation tells that the rate constant is proportional to the proportion of molecules having energy greater than \(E_a\), since the rate is proportional to the number of those molecules. The absolute number (concentration) of those molecules should be a product of \(\exp(-Ea/RT)\) and \([A]\). Therefore, for a reaction from \(A\) to \(B\), the rate \(r\) is

\[
r = [A] \cdot A \exp\left(-\frac{E_a}{RT}\right).
\]
What is "Boltzmann distribution"?

Energy distribution: occupied states
Boltzmann distribution: occupied/unoccupied balance depending on the energy gap between them

\[
\text{(probability of excited state)} = \frac{1}{1 + e^{\frac{-\Delta E}{kT}}}
\]

- \( \Delta E \): energy measured from a standard
- \( k \): Boltzmann constant = \( 1.38 \times 10^{-23} \) J K\(^{-1}\)
- \( T \): absolute temperature = \( 298 \) K (ambient temperature)
- \( kT \): \( 4.11 \times 10^{-21} \) J at ambient temperature
- \( A \): 1 (assumption)
What is "Boltzmann distribution"?

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Boltzmann distribution: occupied/unoccupied balance depending on the energy gap between them

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\( k \) Boltzmann constant = \( 1.38 \times 10^{-23} \) J K\(^{-1}\)
\( T \) absolute temperature = 298 K (ambient temperature)
\( kT \) [4.11 \( \times \) 10\(^{-21}\) J] at ambient temperature
\( A \) 1 (assumption)

if \( \Delta E = 10^{-19} \) J (visible region), the probability is almost 0.
if \( \Delta E = 10^{-20} \) J (infrared region), the probability is ca. 4.5 \( \times \) 10\(^{-5}\)
if \( \Delta E = 10^{-24} \) J (microwave region), the probability is ca. 0.999
time course of a reaction

- Assuming a first-order kinetics, derive the equation of substrate concentration ([A]_t) as a function of time, using a rate constant \( k \), time \( t \) and initial concentration \([A]_0\).
time course of a reaction

• Assuming a first-order kinetics, derive the equation of substrate concentration ([A]_t) as a function of time, using a rate constant \( k \), time \( t \) and initial concentration \([A]_0\).

\[
\frac{r}{-d[A]/dt} = k[A]_t \\
(1/[A]_t)d[A] = -k \, dt \\
\ln [A]_t = -kt + C
\]

• When time = 0, \([A] = [A]_0\). Therefore,

\[
C = \ln [A]_0
\]

\[
[A]_t = [A]_0 \exp(-kt)
\]
Q Draw a time-course curve for a photocatalytic reaction of A obeying a first-order kinetics.
Q. Draw a time-course curve for a photocatalytic reaction of A obeying a first-order kinetics.
first-order kinetics in photocatalysis

Q What kind of mechanism of photocatalytic reaction can interpret the experimental results, if a first-order kinetics, like plots below, is observed?
photocatalytic reaction

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Why first-order kinetics?
comments on this lecture

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太谷文章
某教授
きょうははじめて光触媒について詳しく知りました。光触媒ということばは知っていましたが、実際に応用されている例がたくさんあることに驚きました。光触媒の実際の寿命はどうくらいですか。
「光触媒のしくみがわかる本」を1冊購入します。

JPY1,200 (77%)  JPY3,500 (79%)