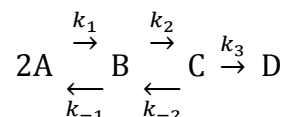


Special Doctoral Program for Green Energy Conversion Science and Technology
Entrance Examination for 2013 (Surface Science)

Question 1

A reaction, $A \rightarrow D$, is supposed to proceed via reaction intermediates of B and C, according to the following equation,



The initial concentration of A is $1.0 \times 10^2 \text{ mol} \cdot \text{L}^{-1}$. The rate constants of forward reaction steps, k_1 , k_2 and k_3 , are $1.0 \text{ mol}^{-1} \cdot \text{L} \cdot \text{s}^{-1}$, 1.0 s^{-1} , and $1.0 \times 10^{-2} \text{ s}^{-1}$, respectively. The rate constants of backward reaction steps, k_{-1} and k_{-2} , are $1.0 \times 10^2 \text{ s}^{-1}$ and $1.0 \times 10^1 \text{ s}^{-1}$, respectively. Answer the following questions.

(1) Let the concentrations of A, B, C and D be [A], [B], [C] and [D], respectively.

Show the consumption rate of A ($= -\frac{1}{2} \frac{d[A]}{dt}$) and the formation rate of B

($= \frac{d[B]}{dt}$), C ($= \frac{d[C]}{dt}$) and D ($= \frac{d[D]}{dt}$) with k_1 , k_2 , k_3 , k_{-1} , k_{-2} , [A], [B], [C] and [D].

(2) On the basis of steady-state approximation for the reaction intermediates B and C, show the consumption rate of A and the formation rate of D with k_1 , k_2 , k_3 , k_{-1} , k_{-2} and [A].

(3) Show [A] as a function of reaction time t .

Question 2

A number of heterogeneous reactions exhibit a maximum rate in the middle of the row of transition metals. Plots of reactivity against periodic table group member with such a maximum are called volcano plots because of their shape. An example is Fisher-Tröpsch (F-T) synthesis of hydrocarbons from synthesis gas using period 4 transition elements as catalysts. In this elemental series, the strength of CO adsorption decreases as atomic number increases. Explain why F-T synthesis exhibits volcano correlation over these elements.

Question 3

For some reactions, catalytic reaction rates over flat (low-indexed) single-crystal surface and over stepped and kinked (high-indexed) surface show marked differences. For instance, the reaction rate of cyclohexane dehydrogenation (reaction 1) over Pt (111) surface is independent of step or kink density on the surface, while the reaction rate of cyclohexane hydrogenolysis (reaction 2) linearly increases with the step or kink density on the surface.



- (1) Conjecture possible active sites on Pt (111) surface for each reaction.
- (2) Pt catalysts are often employed in supported form, dispersed as nano-particles on high-surface-area oxide materials like alumina. In this supported form, Pt nano-particles take shapes like cubo-octahedrons and icosahedrons whose surfaces are composed of low-index flat terraces and ridges between them. Suppose that you have a series of supported Pt catalysts with various Pt particles sizes. State and explain the expected Pt particle size dependence of the reaction rates for the above two reactions.

Question 4

Choose one surface analytical method from the list below, and describe the method in approximately 100 words. Figures may be drawn and used.

Atomic Force Microscopy (AFM)

Auger Electron Spectroscopy (AES)

Electron Microscopy (EM)

Infrared Reflection Absorption Spectroscopy (IRAS)

Low Energy Electron Diffraction (LEED)

Scanning Tunneling Microscopy (STM)

Secondary Ion Mass Spectroscopy (SIMS)

Surface Enhanced Raman Spectroscopy (SERS)

X-ray Absorption Fine Structure (XAFS)

X-ray Photoelectron Spectroscopy (XPS)