ChE445_Seminar6_Winter2020_Solution

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CH E 445 Chemical Reactor Analysis II – Winter 2020
Seminar 6 - Reaction mechanisms of heterogeneous catalytic reactions: Langmuir chemisorption and Langmuir-Hinshelwood model

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Q1. Langmuir adsorption isotherm for a competitive non-dissociative adsorption

Derive Langmuir adsorption isotherms for a competitive non-dissociative adsorption of molecules A and B on the catalyst surface.

$$A + S \rightleftharpoons AS; \ K_A = \frac{\theta_A}{[A]\theta_S} \tag{1}$$

$$B + S \rightleftharpoons BS; \ K_B = \frac{\theta_B}{[B]\theta_S} \tag{2}$$

θ_i is the fraction of surface (Active sites)

Surface balance:

$$\theta_A + \theta_B + \theta_S = 1 \tag{3}$$

$$K_A[A]\theta_S + K_B[B]\theta_S + \theta_S = 1 \tag{4}$$

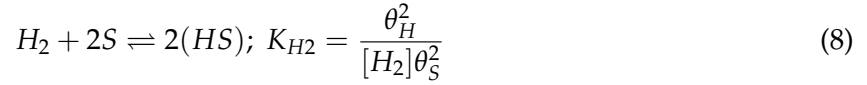$$\theta_S = \frac{1}{K_A[A] + K_B[B] + 1} \tag{5}$$

Then

$$\theta_A = \frac{K_A[A]}{K_A[A] + K_B[B] + 1} \tag{6}$$

$$\theta_B = \frac{K_B[B]}{K_A[A] + K_B[B] + 1} \tag{7}$$

Q 2. Langmuir adsorption isotherm for a monomolecular dissociative adsorption

Derive Langmuir adsorption isotherm for a dissociative adsorption of hydrogen on the Pt catalyst surface.

$$H_2 + 2S \rightleftharpoons 2(HS); \quad K_{H2} = \frac{\theta_H^2}{[H_2]\theta_S^2} \tag{8}$$

θ_i is the fraction of surface (Active sites)
Surface balance:

$$\theta_H + \theta_S = 1 \tag{9}$$
$$\theta_S + \theta_S(K_{H2}[H_2])^{0.5} = 1 \tag{10}$$
$$\theta_S = \frac{1}{1 + (K_{H2}[H_2])^{0.5}} \tag{11}$$

Then

$$\theta_H = \frac{(K_{H2}[H_2])^{0.5}}{1 + (K_{H2}[H_2])^{0.5}} \tag{12}$$

Q 3. Langmuir-Hinshelwood reaction mechanism: bimolecular reaction with nondissociative and dissociative competitive adsorption

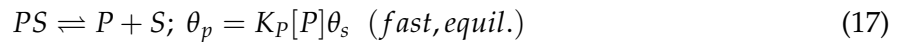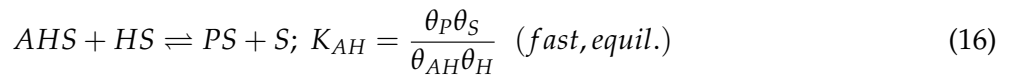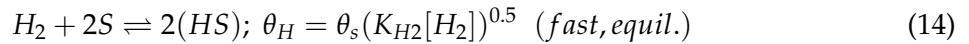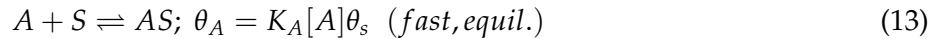Experimental study of a catalytic hydrogenation revealed:
$\frac{1}{2}$ order to H_2,
1st order to the hydrogenated reactant A,
and -2nd order to the product P (or AH_2).

It is suggested that the reaction follows a Langmuir-Hinshelwood mechanism with non-dissociative adsorption of A and P and dissociative adsorption of H_2. Irreversible addition of 1st hydrogen atom to the adsorbed A is an RDS, while the second hydrogen atom addition can be considered fast and in equilibrium.

Derive a rate law and suggest assumptions to satisfy the experimental data.

$$A + S \rightleftharpoons AS; \quad \theta_A = K_A[A]\theta_s \quad (fast, equil.) \tag{13}$$
$$H_2 + 2S \rightleftharpoons 2(HS); \quad \theta_H = \theta_s(K_{H2}[H_2])^{0.5} \quad (fast, equil.) \tag{14}$$
$$AS + HS \rightleftharpoons AHS + S; \quad r = k\theta_H\theta_A \quad (RDS) \tag{15}$$
$$AHS + HS \rightleftharpoons PS + S; \quad K_{AH} = \frac{\theta_P\theta_S}{\theta_{AH}\theta_H} \quad (fast, equil.) \tag{16}$$
$$PS \rightleftharpoons P + S; \quad \theta_p = K_P[P]\theta_s \quad (fast, equil.) \tag{17}$$
$$\tag{18}$$

$$\theta_{AH} = \frac{\theta_P\theta_S}{K_{AH}\theta_S(K_{H2}[H_2])^{0.5}} \tag{19}$$
$$\theta_{AH} = \frac{\theta_P}{K_{AH}(K_{H2}[H_2])^{0.5}} \tag{20}$$

θ_i is the fraction of surface (Active sites)

Surface balance:

$$\theta_A + \theta_H + \theta_{AH} + \theta_P + \theta_S = 1 \tag{21}$$

$$K_A[A]\theta_S + \theta_S(K_{H2}[H_2])^{0.5} + \frac{K_P[P]\theta_S}{K_{AH}K_{H2}[H_2])^{0.5}} + K_P[P]\theta_S + \theta_S = 1 \tag{22}$$

$$\theta_S = \frac{1}{K_A[A] + (K_{H2}[H_2])^{0.5} + \frac{K_P[P]}{K_{AH}K_{H2}[H_2])^{0.5}} + K_P[P] + 1} \tag{23}$$

Then by apply it in RDS

$$r = k\theta_A\theta_H = \frac{kK_A[A](K_{H2}[H_2])^{0.5}}{(K_A[A] + (K_{H2}[H_2])^{0.5} + \frac{K_P[P]}{K_{AH}(K_{H2}[H_2])^{0.5}} + K_P[P] + 1)^2} \tag{24}$$

Can we match it to the experimantal data?

I) 0.5 order to H_2:

nominator: has power 0.5 but to exclude $[H_2]$ from denominator we can assume that surface coverage with H and AH is small, so θ_H and θ_{AH} can be neglected in the surface balance and,

$$r = \frac{kK_A[A](K_{H2}[H_2])^{0.5}}{(K_A[A] + K_P[P] + 1)^2} \tag{25}$$

II) 1st order to $[A]$ and -2nd order to P: So we need $[A]^1$ and $[P]^{-2}$

To match the above rate law we have to assume that $K_P[P] >> K_A[A] + 1$, that is, P is the most abundant surface intermediate and occupied almost all active sites:
Assume: $\theta_P = 1$
Then the RDS reaction rate law will be:

$$r = \frac{kK_A K_{H2}^{0.5}[A][H_2]^{0.5}}{K_P^2[P]^2} \tag{26}$$