CHEG 321: Process Kinetics Due: Friday 10/12/2007

Rate Mechanisms for Catalytic Reactions

1.Consider the hydrogenation of ethylene over Palladium catalyst. From surface-science reports of ethylene and hydrogen adsorption over (111) Pd crystals, the following rate mechanism is proposed:

Overall: $H_2C{=}CH_2 + H_2 \leftrightarrow H_3C{-}CH_3$

$[A] + [B_2] \leftrightarrow [C]$

(1) $A + 2\,S \leftrightarrow S{\cdot}A{\cdot}S$
(2) $B_2 + 2\,S \leftrightarrow 2\,B{\cdot}S$
(3) $S{\cdot}A{\cdot}S + 2\,B{\cdot}S \leftrightarrow S{\cdot}C{\cdot}S + 2\,S$
(4) $S{\cdot}C{\cdot}S \leftrightarrow C + 2\,S$

** assume complete coverage of active sites with either A, B or C (i.e., [S] = 0).

(a) Derive the rate expression for this reaction, assuming that adsorption of A is rate limiting.
(b) Derive the rate expression for this reaction, assuming that adsorption of B is rate limiting.
(c) Derive the rate expression for this reaction, assuming that surface reaction is rate limiting.
(d) Sketch the initial rate of reaction for cases (a), (b), (c) if A_o varies, and B_o and S_t remain constant.
(e) Sketch the initial rate of reaction for cases (a), (b), (c) if B_o varies, and A_o and S_t remain constant.
(f) Sketch the initial rate of reaction for cases (a), (b), (c) if S_t varies, and A_o and B_o remain constant.

2.Consider the isomerization of iso-butane to n-butane, which follows the mechanism,

Overall: $A \leftrightarrow B$

(1) $A + S \leftrightarrow A{\cdot}S$
(2) $A{\cdot}S \leftrightarrow B{\cdot}S$
(3) $B{\cdot}S \leftrightarrow B + S$

Derive the rate expression for this reaction, assuming that there is no rate limiting step, i.e., applying pseudo-steady-state hypothesis to $A{\cdot}S$ and $B{\cdot}S$.

3.Consider the dual-site oxidation of carbon monoxide over Rh-CeO_2, which follows the mechanism:

(1) $CO + O_2 \leftarrow \rightarrow CO_2$
(2) $O_2 + S_1 \leftrightarrow 2\ O{\cdot}S_1$
(3) $CO + S_2 \leftrightarrow CO{\cdot}S_2$
(4) $O{\cdot}S_1 + CO{\cdot}S_2 \leftrightarrow CO_2{\cdot}S_2$
(5) $CO_2{\cdot}S_2 \leftrightarrow CO_2 + S_2$

Derive the rate expression if the surface reaction (4) is rate limiting.