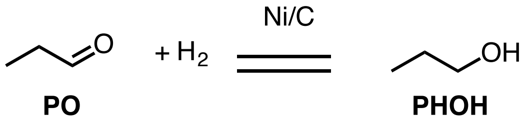
ChE-403 Problem Set 2.4

Week 8

Problem 1

Let's consider the hydrogenation of propanal to propanol over a supported nickel catalyst:



Assume that the rate-limiting step is the reversible chemisorption of PO on the surface and that dihydrogen adsorbs dissociatively on the Ni surface.

Can you propose a complete (and reasonable) sequence of steps and a kinetics expression that satisfies the following experimentally measured rate?

$$r = \frac{cst1\ P_{PO} - cst2\ P_{PHOH}/P_{H_2}}{1 + cst3\ P_{H_2}^{0.5}}$$

Hint: the expression should suggest a simplification to you.

Solution:

The following mechanism can be proposed.

$$\mathrm{PO} + * \overset{A}{\rightleftarrows} \mathrm{PO}^*$$

$$\mathrm{H}_2 + ** \overset{\ominus}{\rightleftarrows} 2\mathrm{H}^*$$

$$\mathrm{PO}^* + \mathrm{H}^* \overset{\ominus}{\rightleftarrows} \mathrm{PHO}^* + *$$

$$\mathrm{PHO}^* + \mathrm{H}^* \overset{\ominus}{\rightleftarrows} \mathrm{PHOH}^* + *$$

$$\mathrm{PHOH}^* \overset{\ominus}{\rightleftarrows} \mathrm{PHOH} + *$$

The first two steps are given and the following steps can be assumed to be at equilibrium because at this point we don't know any better.

The rate expression obtained experimentally strongly suggests that H* is the MARI. Indeed, what is under the fraction bar usually represents what is on the surface and only the expression representing H* is there.

Therefore, let's start with the RDS:

$$r = k_1[PO][*] - k_{-1}[PO*]$$

Let's apply all the equilibria:

$$[PO*] = \frac{[PHO*][*]}{K_3[H*]}$$

$$[PHO*] = \frac{[PHOH*][*]}{K_4[H*]}$$

$$[PHOH*] = \frac{[PHOH][*]}{K_5}$$

We take them all together to get:

$$[PO*] = \frac{[PHOH*][*]^2}{K_3K_4[H*]^2} = \frac{[PHOH][*]^3}{K_3K_4K_5[H*]^2}$$

With:

$$K_2 = \frac{[H*]^2}{[H_2][*]^2}$$

We have:

$$[PO*] = \frac{[PHOH][*]}{K_2K_3K_4K_5[H_2]}$$

With the site balance with H* as the MARI:

$$[*] = [*]_0 - [H*] = [*]_0 - [*](K_2[H_2])^{1/2}$$

$$[*] = \frac{[*]_0}{1 + (K_2[H_2])^{1/2}}$$

With all that, we have:

$$r = k_1[PO][*] - k_{-1}[PO*] = \frac{k_1[PO][*]_0 - \frac{k_{-1}[PHOH][*]_0}{K_2K_3K_4K_5[H_2]}}{1 + (K_2[H_2])^{1/2}}$$

Which is the expression we were looking for…

Problem 2

Consider the following reaction that happens over an activated carbon catalyst:

$$CO + Cl_2 \Rightarrow COCl_2$$

From computational studies it is likely that the rate-limiting step is a surface reaction. From previous studies we know that Cl_2 and $COCl_2$ tend to bind to the catalyst. No information is available for CO. Cl_2 does not dissociate when binding.

Can you propose at least two potential (and reasonable) mechanisms and derive the associated kinetics? Can you suggest a potential experiment that would allow you to differentiate between these two mechanisms?

Solution:

1) An first mechanism could be:

$$\mathrm{Cl_2} + * \xrightleftharpoons{K_1} \mathrm{Cl_2}*$$

$$\mathrm{CO} + * \xrightleftharpoons{K_2} \mathrm{CO}*$$

$$\mathrm{CO}* + \mathrm{Cl_2}* \xrightarrow{k_3} \mathrm{COCl_2}* + *$$

$$\mathrm{COCl_2}* \xrightleftharpoons{K_4} \mathrm{COCl_2} + *$$

Let's write the RDS, which is a Langmuir-Hinshelwood step (see section 2.4.2).

Therefore the kinetics are:

$$r = k_3[CO ** Cl_2] = k_3 \frac{[CO *][Cl_2 *]}{[*]_0}$$

$$[Cl_2 *] = K_1[Cl_2][*]$$

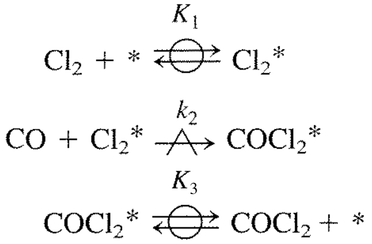
$$[CO *] = K_2[CO][*]$$

$$\begin{aligned}[*] = [*]_0 - [Cl_2 *] - [CO *] - [COCl_2 *]\\ = [*]_0 - K_1[Cl_2][*] - K_2[CO][*] - K_4[COCl_2][*]\end{aligned}$$

$$[*] = \frac{[*]_0}{1 + K_1[Cl_2] + K_2[CO] + K_4[COCl_2]}$$

$$r = \frac{k_3 K_2 K_1 [*]_0 [Cl_2][CO]}{(1 + K_1[Cl_2] + K_2[CO] + K_4[COCl_2])^2}$$

2) A second possible mechanism could be an Eley Rideal mechanism with CO (because we don't know if it is actually present on the surface):



$$Cl_2 + * \overset{K_1}{\rightleftharpoons} Cl_2*$$

$$CO + Cl_2* \xrightarrow{k_2} COCl_2*$$

$$COCl_2* \overset{K_3}{\rightleftharpoons} COCl_2 + *$$

In this case the RDS is simpler:

$r = k_3[CO][Cl_2 *]$

$[Cl_2 *]$ is given by the same expressions as above (except that there is no CO on the surface so it does not appear in the site balance):

$$[Cl_2 *] = K_1[Cl_2][*] = \frac{K_1[*]_0[Cl_2]}{1 + K_1[Cl_2] + K_3[COCl_2]}$$

$$r = \frac{k_3K_1[*]_0[Cl_2][CO]}{1 + K_1[Cl_2] + K_3[COCl_2]}$$

You could differentiate using any experiment in which you varied $[Cl_2]$, $[CO]$ and $[COCl_2]$ and fit the rate data to see which expression fit. A particularly easy experiment would be to work at high CO pressure compared to the other components and see if $r \propto 1/[CO]$ (case 1) or $r \propto [CO]$ (case 2).