# Catalysis – continue (Adsorption resistance controlling)

## For the catalytic reaction $A + B \Leftrightarrow C$

**We will have four main intermediate steps; adsorption of A and B by the surface of the catalyst, surface reaction of both adsorbed A and B, and desorption of the produced C from the surface of the catalyst.**

**This class we will consider the adsorption of A is the controlling step:**

Adsorption (controlling)

$$A + X \leftrightarrow A * X$$

$$B + X \leftrightarrow B * X$$

Surface Reaction

$$A * X + B * X \leftrightarrow C * X + X$$

Desorption

$$C * X \leftrightarrow C + X$$

The rate of reaction for controlling step (Adsorption of A) is

$$-r_{Ads.A} = k_{Af}\left(C_A\, C_v - \frac{C_{A*X}}{K_A}\right)$$

But the surface concentration for B and C were developed previously as

$$C_{B*X} = K_B C_B C_v$$

$$C_{C*X} = K_C C_C C_v$$

But from the surface reaction step we have:

$$K_S = \frac{C_{C*X} C_v}{C_{A*X}\, C_{B*X}} \quad \Longrightarrow \quad C_{A*X} = \frac{C_{C*X} C_v}{K_S\, C_{B*X}} = \frac{K_C C_C C_v\, C_v}{K_S K_B C_B C_v} = \frac{K_C C_C C_v}{K_S K_B C_B}$$

The site balance is

$$C_T = C_{A*X} + C_{B*X} + C_{C*X} + C_v$$

or

$$C_T = \frac{K_C C_C C_v}{K_S K_B C_B} + K_B C_B C_v + K_C C_C C_v + C_v$$

$$C_T = C_v \left( \frac{K_C C_C}{K_S K_B C_B} + K_B C_B + K_C C_C + 1 \right)$$

$$C_v = \frac{C_T}{\left( \frac{K_C C_C}{K_S K_B C_B} + K_B C_B + K_C C_C + 1 \right)}$$

$$-r_{Ads.A} = k_{Af} \left( C_A \, C_v - \frac{C_{A*X}}{K_A} \right) = k_{Af} \left( C_A \, C_v - \frac{\frac{K_C C_C C_v}{K_S K_B C_B}}{K_A} \right) = k_{Af} C_v \left( C_A - \frac{K_C}{K_A K_S K_B} \frac{C_C}{C_B} \right)$$

$$-r_{Ads.A} = k_{Af} C_v \left(C_A - \frac{K_C}{K_A K_S K_B} \frac{C_C}{C_B}\right) \qquad C_v = \frac{C_T}{\left(\frac{K_C C_C}{K_S K_B C_B} + K_B C_B + K_C C_C + 1\right)}$$

$$-r_{Ads.A} = k_{Af} \frac{C_T}{\left(\frac{K_C C_C}{K_S K_B C_B} + K_B C_B + K_C C_C + 1\right)} \left(C_A - \frac{K_C}{K_A K_S K_B} \frac{C_C}{C_B}\right)$$

or

$$-r_{Ads.A} = k_{Af} C_T \frac{\left(C_A - \frac{K_C}{K_A K_S K_B} \frac{C_C}{C_B}\right)}{\left(\frac{K_C C_C}{K_S K_B C_B} + K_B C_B + K_C C_C + 1\right)}$$

# Catalysis – continue (Desorption resistance controlling)

Adsorption

$$A + X \leftrightarrow A * X$$
$$B + X \leftrightarrow B * X$$

Surface Reaction

$$A * X + B * X \leftrightarrow C * X + X$$

Desorption (controlling)

$$C * X \leftrightarrow C + X$$

The rate of reaction for controlling step (Desorption of C) is

$$-r_{Des.C} = k_{cf}\left(C_{C*X} - \frac{C_C\, C_v}{K_C}\right)$$

But the surface concentration for A and B were developed previously as

$$C_{B*X} = K_B C_B C_v$$
$$C_{A*X} = K_A C_A C_v$$

And the surface equilibrium reaction

$$K_S = \frac{C_{C*X} C_v}{C_{A*X}\, C_{B*X}}$$

Re-arrange to get

$$C_{C*X} = \frac{K_S\, C_{A*X}\, C_{B*X}}{C_v}$$

$$C_{B*X} = K_B C_B C_v$$

$$C_{A*X} = K_A C_A C_v$$

$$C_{C*X} = \frac{K_S\, K_A C_A C_v\;\; K_B C_B C_v}{C_v}$$

or $C_{C*X} = K_S\, K_A K_B\, C_A\, C_B\, C_v$

$$-r_{Des.C} = k_{cf}\left(K_S\, K_A K_B\, C_A\, C_B\, C_v - \frac{C_C\, C_v}{K_C}\right)$$

$$-r_{Des.C} = k_{cf} C_v\left(K_S\, K_A K_B\, C_A\, C_B - \frac{C_C}{K_C}\right)$$

The site balance is

$$C_{C*X} = K_S\, K_A K_B\, C_A\, C_B\, C_v$$

$$C_T = C_{A*X} + C_{B*X} + C_{C*X} + C_v$$

or

$$C_T = K_A C_A C_v + K_B C_B C_v + K_S\, K_A K_B\, C_A\, C_B\, C_v + C_v$$

$$C_T = C_v\,(K_A C_A + K_B C_B + K_S\, K_A K_B\, C_A\, C_B + 1)$$

$$C_v = \frac{C_T}{(K_A C_A + K_B C_B + K_S\, K_A K_B\, C_A\, C_B + 1)}$$

Substitute the vacant site in the rate equation

$$-r_{Des.C} = k_{cf} C_v \left( K_S\, K_A K_B\, C_A\, C_B - \frac{C_C}{K_C} \right)$$

$$-r_{Des.C} = k_{cf} \frac{C_T}{(\, K_A C_A + K_B C_B + K_S\, K_A K_B\, C_A\, C_B + 1)} \left( K_S\, K_A K_B\, C_A\, C_B - \frac{C_C}{K_C} \right)$$

$$-r_{Des.C} = k_{cf}\, C_T \frac{\left( K_S\, K_A K_B\, C_A\, C_B - \frac{C_C}{K_C} \right)}{(\, K_A C_A + K_B C_B + K_S\, K_A K_B\, C_A\, C_B + 1)}$$

## Conclusion

- If the denominator in the rate expression is raised to a power of 2 and contains the expressions $K_A C_A$, $K_B C_B$, and $K_C C_C$, then the controlling step is surface reaction of type I
- If the denominator contains only $K_A C_A$ and $K_C C_C$, then the controlling step is surface reaction of type II where B is reacted in gas phase with adsorbed A
- If the denominator contains a fraction of concentration of a species with respect to other species such as $\frac{C_C}{C_B}$, then adsorption of the remaining species is controlling, here the remaining species is A
- If the denominator contains multiplication of concentration of more than one species such as $C_A C_B$, then a desorption step of the remaining species is controlling. Here the desorption step of the missing species C is the controlling.