Lecture Heterogeneous Catalysis
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Script available:
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Outline

1. Introduction (1)
2. Modern concepts in catalysis research (2)
3. Catalyst synthesis (3, 4, 5)
4. Characterization of solid catalysts (6, 7, 8)
5. Kinetics (9, 10)
6. Important technical processes (11, 12, 13)
7. Reaction mechanism and catalyst’s dynamics – case studies (14, 15)
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5. Kinetics II

5.1. Kinetics - Introduction
5.2. Kinetic description of chemical reactions
5.3. Determination of kinetics
5.4. Reaction and transport phenomena
5.5. Surface reactivity / Kinetics of reactions at surfaces
5.6. Ammonia synthesis
5.7. General concepts and determination of the reaction mechanism
5. Kinetics II

Literature
5.5 Catalytic reactions at surfaces

Schematic representation of the simplest possible reaction in heterogeneous catalysis

Simplifying assumptions:
- In terms of kinetics, the catalyst must be included as a participating species that leaves the reaction unaltered
- A collection of active sites (*) is present at the catalyst surface
- All sites are equivalent and each can be occupied by a single species only

Mean field approximation:
- All adsorbed species are distributed randomly over the surface
- There is no interaction between the adsorbed species
Catalytic reactions at surfaces

Figure 2.8. Checker board model of a surface with two adsorbates; left: randomly distributed; right: attractive interactions give rise to islands of B. In the latter case reaction between A and B is only possible at the perimeter of the island, hence the rate is no longer proportional to the coverage of B.

(1), p.52
Catalytic reactions at surfaces

Adsorption isotherms: basis of the kinetics at catalyst surfaces

\[
A + * \xrightleftharpoons{\kappa_A^+}{\kappa_A^-} A^* \\

\frac{d\theta_A}{dt} = p_A k_A^+ (1 - \theta_A) - k_A^- \theta_A \\

K_A = \frac{k_A^+}{k_A^-} \\
\]

in equilibrium:

\[
p_A k_A^+ (1 - \theta_A) = k_A^- \theta_A \\
\theta_A = \frac{K_A p_A}{1 + K_A p_A} \\
\theta_\ast = (1 - \theta_A) = \frac{1}{1 + K_A p_A} \quad \Rightarrow \quad \theta_A = K_A p_A \theta_\ast
\]

Irving Langmuir
Nobel Prize in Chemistry in 1932
Catalytic reactions at surfaces

Dissociative adsorption
(Adsorption of \( \text{H}_2 \) or \( \text{O}_2 \))

\[
\begin{align*}
\text{A}_2 + 2 * & \underset{k_A^-}{\overset{k_A^+}{\rightleftharpoons}} 2 \text{A}^* \\
\end{align*}
\]

\[
\frac{d\theta_A}{dt} = p_A^2 k_A^+ (1 - \theta_A)^2 - k_A^- \theta_A^2
\]

in equilibrium:

\[
p_A^2 k_A^+ (1 - \theta_A)^2 = k_A^- \theta_A^2
\]

\[
\theta_A = \frac{\sqrt{K_A^2 p_A^2}}{1 + \sqrt{K_A^2 p_A^2}}
\]

\[
\theta_* = \frac{1}{1 + \sqrt{K_A^2 p_A^2}}
\]

Competitive adsorption

\[
\begin{align*}
\text{A} + * & \underset{K_A}{\overset{K_A}{\rightleftharpoons}} \text{A}^* \\
\text{B} + * & \underset{K_B}{\overset{K_B}{\rightleftharpoons}} \text{B}^* \\
\end{align*}
\]

\[
\theta_A = K_A p_A \theta_* , \theta_B = K_B p_B \theta_*
\]

\[
\theta_A + \theta_B + \theta_* = 1
\]

\[
\theta_A = \frac{K_A p_A}{1 + K_A p_A + K_B p_B}
\]

\[
\theta_B = \frac{K_B p_B}{1 + K_A p_A + K_B p_B}
\]

\[
\theta_* = \frac{1}{1 + K_A p_A + K_B p_B}
\]
Langmuir-Hinshelwood kinetics

Monomolecular surface reaction

\[
\begin{align*}
A^* & \xrightarrow{k_s} B^* \\
\theta_A = k_s p_A & = \frac{K_A p_A}{1 + K_A p_A} \\
\end{align*}
\]

Bimolecular surface reaction

\[
\begin{align*}
A^* + B^* & \xrightarrow{k_s} AB^* \\
r = k_s \theta_A \theta_B & = \frac{k' p_A p_B}{(1 + K_A p_A + K_B p_B)^2}, \quad k' = k_s K_A K_B \\
\end{align*}
\]

Case a: \( r = k_s \theta_A \theta_B \)

\[
r = \frac{k' p_A p_B}{(1 + K_A p_A + K_B p_B)^2}, \quad k' = k_s K_A K_B
\]

Case b: \( r = k_s \theta_A p_B \)

\[
r = \frac{k' p_A p_B}{1 + K_A p_A}, \quad k' = k_s K_A
\]

Abb. 4.1.2. Abhängigkeit der Geschwindigkeit einer Reaktion
\( A_1 + A_2 \rightarrow A_3 \) vom Partialdruck der Komponente \( A_1 \), bei konstantem Partialdruck an \( A_2 \)

- a Langmuir-Hinshelwood Kinetik nach Gl. (4.86)
- b Eley-Rideal Kinetik nach Gl. (4.89)

(Parameterwerte: \( k = 10^{-15} \text{ mol Pa}^{-2} \text{ g}^{-1} \text{ s}^{-1}, \ K_1 = 0,9 \cdot 10^{-5} \text{ Pa}, \ K_2 = 0,3 \cdot 10^{-5} \text{ Pa} \))
5.5 Complex surface reactions

We assume that the elementary steps are known

(1) $\text{A} + \ast \xrightarrow{k_1^+} \text{A}^* \quad r_1 = k_1^+ p_A \theta_* - k_1^- \theta_A$

(2) $\text{B} + \ast \xrightarrow{k_2^+} \text{B}^* \quad r_2 = k_2^+ p_B \theta_* - k_2^- \theta_B$

(3) $\text{A}^* + \text{B}^* \xrightarrow{k_3^+} \text{AB}^* + \ast \quad r_3 = k_3^+ \theta_A \theta_B - k_3^- \theta_{AB} \theta_*$

(4) $\text{AB}^* \xrightarrow{k_4^+} \text{AB} + \ast \quad r_4 = k_4^+ \theta_{AB} - k_4^- p_{AB} \theta_*$

Assumption: site balance $\theta_* + \theta_A + \theta_B + \theta_{AB} = 1, \quad \sum_{i=1}^{n} \theta_i = 1$

The catalyst is unaltered by the reaction (the number of sites on a catalyst is constant)
Complex surface reactions

1. Complete solution to describe the transient time dependent kinetic behaviour

(1) \[ A + * \overset{k_1^+}{\underset{k_1^-}{\rightleftharpoons}} A^* \quad \frac{d\theta_A}{dt} = r_1 - r_3 = k_1^+ p_A \theta_* - k_3^- \theta_A - k_3^+ \theta_A \theta_B + k_3^- \theta_{AB} \theta_* \]

(2) \[ B + * \overset{k_2^+}{\underset{k_2^-}{\rightleftharpoons}} B^* \quad \frac{d\theta_B}{dt} = r_2 - r_3 = k_2^+ p_B \theta_* - k_3^- \theta_B - k_3^- \theta_A \theta_B + k_3^- \theta_{AB} \theta_* \]

(3) \[ A^* + B^* \overset{k_3^+}{\underset{k_3^-}{\rightleftharpoons}} AB^* + * \quad \frac{d\theta_{AB}}{dt} = r_3 - r_4 = k_3^+ \theta_A \theta_B - k_3^- \theta_{AB} \theta_* - k_4^- \theta_{AB} + k_4^+ p_{AB} \theta_* \]

(4) \[ AB^* \overset{k_4^+}{\underset{k_4^-}{\rightleftharpoons}} AB + * \quad \frac{d\theta_\ast}{dt} = -r_1 - r_2 + r_3 + r_4 \]

Numerical solution requires that all kinetic parameters are known or estimated.
Complex surface reactions

2. Steady-state approximation

\[
0 = \frac{d\theta_A}{dt} = r_1 - r_3 = k_1^+ p_A \theta_* - k_1^- \theta_A - k_3^+ \theta_A \theta_B + k_3^- \theta_{AB} \theta_*
\]

\[
0 = \frac{d\theta_B}{dt} = r_2 - r_3 = k_2^+ p_B \theta_* - k_2^- \theta_B - k_3^+ \theta_A \theta_B + k_3^- \theta_{AB} \theta_*
\]

\[
0 = \frac{d\theta_{AB}}{dt} = r_3 - r_4 = k_3^+ \theta_A \theta_B - k_3^- \theta_{AB} \theta_* - k_4^+ \theta_{AB} + k_4^- p_{AB} \theta_*
\]

\[
0 = \frac{d\theta_*}{dt} = -r_1 - r_2 + r_3 + r_4
\]

\[
\theta_* + \theta_A + \theta_B + \theta_{AB} = 1, \quad \sum_{i=1}^{n} \theta_i = 1
\]

The last equation is not independent of the others due to the site balance \( \rightarrow \) n-1 equation for a reaction containing n elementary steps
Complex surface reactions

2. Quasi-equilibrium approximation: rds is the surface reaction (3)

(1) \[ A + * \xrightleftharpoons[k_1^-]{k_1^+} A^* \]

\[ r_1 \equiv 0 \Rightarrow k_1^+ p_A \theta_* = k_1^- \theta_A \Rightarrow \theta_A = K_1 p_A \theta_* \]

(2) \[ B + * \xrightleftharpoons[k_2^-]{k_2^+} B^* \]

\[ r_2 \equiv 0 \Rightarrow k_2^+ p_B \theta_* = k_2^- \theta_B \Rightarrow \theta_B = K_2 p_B \theta_* \]

(3) \[ A^* + B^* \xrightleftharpoons[k_3^-]{k_3^+} AB^* + * \]

\[ r_3 = k_3^+ \theta_A \theta_B - k_3^- \theta_{AB} \theta_* \]

(4) \[ AB^* \xrightleftharpoons[k_4^-]{k_4^+} AB + * \]

\[ r_4 \equiv 0 \Rightarrow k_4^+ \theta_{AB} = k_4^- p_{AB} \theta_* \Rightarrow \theta_{AB} = K_4^{-1} p_{AB} \theta_* \]
Complex surface reactions

2. Quasi-equilibrium approximation: rds is the surface reaction (3)

\[
r = r_3 = k_3^+ K_1 K_2 p_A p_B \left(1 - \frac{p_{AB}}{p_A p_B K_1 K_2 K_3 K_4}\right) \theta_*^2
\]

\[
r = r^+ - r^- = k_3^+ K_1 K_2 p_A p_B \left(1 - \frac{p_{AB}}{p_A p_B K_G}\right) \theta_*^2, \quad K_G = K_1 K_2 K_3 K_4
\]

\[
\theta_* = \frac{1}{1 + K_1 p_A + K_2 p_B + K_4^{-1} p_{AB}}, \quad \theta_* = 1 - \theta_A + \theta_B + \theta_{AB}
\]

\[
r = r^+ - r^- = k_3^+ K_1 K_2 p_A p_B \left(1 - \frac{p_{AB}}{p_A p_B K_G}\right) \left(1 \frac{1}{1 + K_1 p_A + K_2 p_B + K_4^{-1} p_{AB}}\right)^2
\]

The rds might shift to another step if reaction conditions change.
Complex surface reactions

3. Irreversible step approximation

The desorption of the product AB is irreversible, $p_{AB} = 0$

$$r = r^+ - r^- = k_3^+ K_1 K_2 p_A p_B \left( 1 - \frac{p_{AB}}{p_A p_B K_G} \right) \frac{1}{\left( 1 + K_1 p_A + K_2 p_B + K_4^{-1} p_{AB} \right)^2}$$

$$r = r_3 = r^+ = \frac{k_3^+ K_1 K_2 p_A p_B}{\left( 1 + K_1 p_A + K_2 p_B \right)^2}$$
Complex surface reactions

4. Most Abundant Reaction (Surface) Intermediate (MAR(S)I) approximation

Often, one intermediate (MARI) adsorbs so strongly compared to the other participants that it dominates the surface completely:

$$\sum_{i=1}^{n} \theta_i \approx \theta_* + \theta_{MARI} = 1$$

Quasi-equilibrium approximation:

$$r = r^+ - r^- = k_3^+ K_1 K_2 p_A p_B \left(1 - \frac{p_{AB}}{p_A p_B K_G} \right) \left(\frac{1}{1 + K_1 p_A + K_2 p_B + K_4^{-1} p_{AB}} \right)^2$$

$$\theta_A \equiv \frac{K_1 p_A}{1 + K_1 p_A}, \; \theta_B \equiv 0, \; \theta_{AB} \equiv 0, \; \theta_* \equiv 1 - \theta_A$$

$$r = r^+ - r^- = k_3^+ K_1 K_2 p_A p_B \left(1 - \frac{p_{AB}}{p_A p_B K_G} \right) \left(\frac{1}{1 + K_1 p_A} \right)^2$$
Complex surface reactions

Example CO oxidation (quasi equilibrium approximation)

(1) \[ CO + * \rightleftharpoons K_1 CO^* \]

(2) \[ O_2 + 2* \rightleftharpoons K_2 2O^* \] (composed of several steps)

(3) \[ CO^* + O^* \rightleftharpoons k_3^+ CO_2^* + * \] (rds)

(4) \[ CO_2^* \rightleftharpoons K_4^{-1} CO_2 + * \]

- Catalyst: noble metal, such as Pt, Pd, Rh, Ir, Au (small particles)
- Reaction is an important step in automotive exhaust catalysis
- Subject of numerous fundamental studies
Complex surface reactions

Example CO oxidation (quasi equilibrium approximation)

1. \[ CO + * \rightleftharpoons CO^* \]
   \[ \theta_{CO} = K_1 p_{CO} \theta_* \]

2. \[ O_2 + 2* \rightleftharpoons 2O^* \]
   \[ \theta_O = \sqrt{K_2 p_{O2}} \theta_* \]

3. \[ CO^* + O^* \rightleftharpoons CO_2^* + * \]
   \[ k_3^+ \]
   \[ k_3^- \]

4. \[ CO_2^* \rightleftharpoons CO_2 + * \]
   \[ \theta_{CO_2} = K_4^{-1} p_{CO_2} \theta_* \]

\[ \theta_{CO} + \theta_O + \theta_{CO_2} + \theta_* = 1 \Rightarrow \theta_* = \frac{1}{1 + K_1 p_{CO} + \sqrt{K_2 p_{O2}} + K_4^{-1} p_{CO_2}} \]
Complex surface reactions

Example CO oxidation (quasi equilibrium approximation)

\[ \theta_{CO} + \theta_{O} + \theta_{CO_2} + \theta_* = 1 \Rightarrow \theta_* = \frac{1}{1 + K_1 p_{CO} + \sqrt{K_2 p_{O_2} + K_4^{-1} p_{CO_2}}} \]

\[
\begin{align*}
\text{CO} + \frac{1}{2} \text{O}_2 & \overset{K_G}{\rightleftharpoons} \text{CO}_2 \\
k^+ & \\
k^- & \\
\end{align*}
\]

(3)

\[ r = k^+_3 \theta_{CO} \theta_{O} - k^-_3 \theta_{CO_2} \theta_* \]

\[ r = k^+_3 K_1 \sqrt{K_2} p_{CO} \sqrt{p_{O_2}} \left(1 - \frac{p_{CO_2}}{p_{CO} \sqrt{p_{O_2} K_G}} \right) \theta_*^2, \ K_G = K_1 \sqrt{K_2 K_3 K_4} \]
Example CO oxidation (quasi equilibrium approximation)

\[ r = k_3^+ K_1 \sqrt{K_2 p_{\text{CO}}} \sqrt{p_{\text{O}_2}} \left( 1 - \frac{p_{\text{CO}_2}}{p_{\text{CO}} \sqrt{p_{\text{O}_2} K_G}} \right) \theta_*^2, \quad K_G = K_1 \sqrt{K_2 K_3 K_4} \]

- CO\textsubscript{2} weakly interacts with the surface \(\Rightarrow\) terms containing \(p_{\text{CO}_2}=0\)
- At low T the surface is covered by CO \(\Rightarrow\) CO is MARI

\[ \theta_* = \frac{1}{1 + K_1 p_{\text{CO}}} \approx \frac{1}{K_1 p_{\text{CO}}}, \quad \text{if} \quad K_1 p_{\text{CO}} >> 1 \]

\[ r = \frac{k_3^+ \sqrt{K_2 p_{\text{O}_2}}}{K_1 p_{\text{CO}}}, \quad n_{\text{O}_2} = 0.5, \quad n_{\text{CO}} = -1 \]

- Further increase in CO pressure will reduce the rate, because sites for oxygen adsorption are blocked
Complex surface reactions

Example CO oxidation (quasi equilibrium approximation)

\[ r = k_3^+ K_1 \sqrt{K_2 p_{CO}} \sqrt{p_{O_2}} \left( 1 - \frac{p_{CO_2}}{p_{CO} \sqrt{p_{O_2} K_G}} \right) \theta_*^2, \quad K_G = K_1 \sqrt{K_2 K_3 K_4} \]

- CO\textsubscript{2} weakly interacts with the surface \( \Rightarrow \) terms containing \( p_{CO_2} = 0 \)
- At high \( T \) the surface is nearly empty

\[ \theta_* \approx 1, \quad r = k_3^+ K_1 \sqrt{K_2 p_{CO}} \sqrt{p_{O_2}}, \quad n_{O_2} = 0.5, \quad n_{CO} = +1 \]

- Because the surface is predominately empty, increasing the partial pressure of both reactants leads to an increase in the rate
Kinetics at surfaces

CO oxidation, $K_{CO} = 1$ at 650 K, $\Delta H_{CO} = -135 \text{kJ/mol}$
$K_{O_2} = 1$ at 630 K, $\Delta H_{O_2} = -250 \text{kJ/mol}$, $K_{CO_2}$ small,
$k = 1$ at 540 K, $E_a = 50 \text{kJ/mol}$, $P_{O_2} = 10^*P_{CO}$, and $P_{CO} = 1$

Key:
Right amount of reacting species on the catalyst surface at the right temperature
For complex reactions:
Screen the parameter field to find optimized reaction conditions

Figure 2.12. Coverage of CO and O and the rate for CO oxidation as a function of temperature (upper panel). The lower panel displays both the reaction order and the overall activation energy as function of temperature. Any influence of CO$_2$ has been ignored.
Mars-van-Krevelen

\[ R + O_{O,s}^x \rightarrow P + V_{O,s}^* \quad r_1 = k_1 p_R \theta_O \]  \hspace{1cm} (1)

\[ V_{O,s}^* + \frac{1}{2} O_2 \rightarrow O_{O,s}^x \quad r_2 = k_2 p_{O_2}^n (1 - \theta_O) \]  \hspace{1cm} (2)

\[ R + \frac{1}{2} O_2 \rightarrow P \quad \text{overall reaction rate } r \]  \hspace{1cm} (3)

\[ r_1 = \frac{r_2}{\beta} \]  \hspace{1cm} (4)

\[ \text{steady state: } \beta k_1 p_R \theta_O = k_2 p_{O_2}^n (1 - \theta_O) \]  \hspace{1cm} (5)

\[ \theta_O = \frac{k_2 p_{O_2}^n}{\beta k_1 p_R + k_2 p_{O_2}^n} \]  \hspace{1cm} (6)

\[ r = \frac{k_1 k_2 p_R p_{O_2}^n}{k_1 p_R + k_2 p_{O_2}^n} \]  \hspace{1cm} (7)

- \( R \): hydrocarbon
- \( O_{O,s}^x \): regular lattice oxygen atom at the catalyst surface
- \( P \): Product of selective oxidation reaction
- \( V_{O,s}^* \): doubly charged oxygen vacancy at the surface of the catalyst
- \( r_1, k_1 \): rate and rate constant of reaction (1) (reduction of the catalyst)
- \( r_2, k_2 \): rate and rate constant of reaction (2) (reoxidation of the catalyst)
- \( \theta_O \): fraction of reacting lattice O ions at the surface
- \( \beta \): number of oxygen molecules required to oxidize one hydrocarbon molecule
Hougen-Watson rate equations

Compilation of examples that describe different types of reactions (different rds, different equilibria)

\[ r = \frac{(\text{kinetischer Term})(\text{Potenzialterm})}{(\text{Adsorptionsterm})^n} \]

5.6. Ammonia synthesis

\[ \text{N}_2 + 3 \text{H}_2 \leftrightarrow 2 \text{NH}_3 \]

We need a catalyst!

“The agriculture of the world has been supplied with fertilizers rich in nitrogen since 1913 due to the Haber-Bosch process, where the nitrogen of the air is converted to ammonia using an iron-based catalyst.”
(Royal Swedish Academy of Science, 2007)

Ammonia synthesis

\[ \text{N}_2 + 3 \text{H}_2 \rightleftharpoons 2 \text{NH}_3 \]

Catalyst: multicomponent system composed of Fe (prepared from Fe\(_3\)O\(_4\)) promoted with K\(_2\)O, Al\(_2\)O\(_3\), and CaO

Paul Alwin Mittasch, Leiter des Ammoniaklabors der BASF

Nobelpreise in Chemie

Fritz Haber 1918
Carl Bosch 1931
Gerhard Ertl 2007
5.6

The surface of the iron catalyst

J.M. Thomas, W.J. Thomas, "Principles and Practice of Heterogeneous Catalysis" (VCH)

- Reduction at 400°C in the feed results in the formation of small α-Fe particles
- The catalyst is porous
- Al₂O₃ and CaO act as structural promoters and prevent sintering of α-Fe particles
- It is assumed that metallic Fe is the crucial catalytically active surface component
- Clean Fe single-crystal surfaces (Fe(111)) are legitimate starting points for model studies
- The role of K₂O as electronic promoter is studied separately


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The rate-determining step

Investigation of molecular and real catalysts (XPS, AES, LEED, TDS)

Molecular route: \( \text{N}_2 \text{(ad)} + 6 \text{H} \text{(ad)} \rightarrow 2 \text{NH}_3 \)

Atomic route: \( \text{N} \text{(ad)} + 3 \text{H} \text{(ad)} \rightarrow \text{NH}_3 \)

Desorption experiments:

\[
\begin{align*}
\text{H}_2 & \quad \xrightleftharpoons[K_1]{K_2} \quad 2 \text{H}_{\text{ads}} & \quad T_{\text{des}} \leq 200^\circ \text{C} \\
\text{N}_2 & \quad \xrightleftharpoons[k_3]{\text{N}_2,\text{ads}} & \quad T_{\text{des}} \leq -100^\circ \text{C} \\
\text{N}_2,\text{ads} & \quad \xrightleftharpoons[k_3]{2 \text{N}_{\text{ads}}} & \quad T_{\text{des}} > 450^\circ \text{C} \\
\text{NH}_3 & \quad \xrightleftharpoons[\text{NH}_3,\text{ads}]{\text{NH}_3,\text{ads}} & \quad T_{\text{des}} > 450^\circ \text{C}
\end{align*}
\]

\[
\frac{d[N_{\text{ads}}]}{dt} = k_3[N_{2,\text{ads}}] - k[N_{\text{ads}}][H_{\text{ads}}]^y = k_3 K_2 p_{N_2} - kK_1[N_{\text{ads}}]p_{H_2}^x
\]

\[
[N_{\text{ads}}]_{\text{stat}} = k' \frac{p_{N_2}^x}{p_{H_2}^x}
\]

\( x \) is an unknown (variable) exponent including the reaction order \( y \) and the type of adsorption isotherm correlating \([H_{\text{ad}}]\) with \( p_{H_2} \)
The rate-determining step

Molecular route: \[ N_2 \text{(ad)} + 6 \text{H (ad)} \rightarrow 2 \text{NH}_3 \]

Atomic route: \[ N \text{(ad)} + 3 \text{H (ad)} \rightarrow \text{NH}_3 \]

\[
\frac{d[N_{ads}]}{dt} = k_3[N_{2,ads}] - k[N_{ads}][H_{ads}]^y
\]

\[
= k_3 K_2 p_{N_2} - k K_1 [N_{ads}] p_{H_2}^x
\]

\[
[N_{ads}]_{stat} = k' \frac{p_{N_2}^{x}}{p_{H_2}^x}
\]

**FIG. 3.** Steady-state surface concentration of atomic nitrogen on a Fe(111) surface as a function of H$_2$ pressure at T = 310°C and p$_{N_2}$ = 150 Torr.

How is nitrogen adsorbed?

- Adsorption energy of molecular nitrogen $\approx 10$ kcal/mol
- Preferential molecular adsorption at low T, preferential atomic adsorption at high T
- Dissociative nitrogen adsorption is a very slow process (sticking coefficient $10^{-8} - 10^{-10}$)
- The sticking coefficient $s$ describes how many of the incident atoms were successful in reaching the adsorbed state

$$s = \left( \frac{\text{rate of adsorption}}{\text{rate of bombardment}} \right)$$

FIG. 6. Lennard-Jones potential diagram for molecular and atomic nitrogen adsorption on a clean (a) and a potassium-covered (b) Fe(100) surface.

Surface nitride (similar to bulk nitride Fe$_4$N)

How is nitrogen adsorbed?

- The slope of the adsorption isotherms are proportional to the rate of dissociative nitrogen adsorption
- The corresponding activation energy is very small and depends on coverage (repulsive interaction in the adsorbate layer) and surface structure (≈5 kcal/mol)
- Despite the low activation energy, only a very small fraction of about $10^{-6}$ of those molecules whose thermal energy exceeds $E_a$ is dissociatively adsorbed
- It seems that the activation entropy for this process is rather unfavourable

How is hydrogen adsorbed?

- The sticking coefficient of hydrogen is high (0.1 - 0.2)
- The surface mobility of adsorbed hydrogen is much higher than that of nitrogen atoms
- At temperatures above 400°C the concentration of adsorbed hydrogen atoms is small and unlikely to inhibit adsorption of nitrogen

FIG. 4. Series of thermal desorption spectra for H₂ at a Fe(111) surface. The parameter is the H₂ exposure (1 L = 10⁻⁶ Torr·sec).
Interaction with ammonia

Thermal desorption of ammonia is completed at 100°C so that this process will be very rapid at the temperature of the synthesis.

NH₃ decomposition takes place at elevated temperatures.

FIG. 11. Thermal desorption spectra for NH₃ (a) and NH₂D (b) from a Fe(111) surface which had been exposed to D₂ and NH₃ at 135°K.
The reaction mechanism

Elementary steps (7) at the surface of iron:

\[
\begin{align*}
H_2 & \rightleftharpoons 2 H_{ads} \\
N_2 & \rightleftharpoons N_{2,ads} \rightleftharpoons 2 N_{ads} \\
N_{ads} + H_{ads} & \rightleftharpoons NH_{ads} \\
NH_{ads} + H_{ads} & \rightleftharpoons NH_{2,ads} \\
NH_{2,ads} + H_{ads} & \rightleftharpoons NH_{3,ads} \rightleftharpoons NH_3
\end{align*}
\]
## Microkinetic model

\[
\begin{align*}
\frac{d\theta_{N_2}}{dt} &= p_{N_2} k^+_1 \theta^*_N - k^-_1 \theta_{N_2} = 0 \Rightarrow \theta_{N_2} = K_1 p_{N_2} \theta_* \\
r &= r^+ - r^- = k^+_2 \theta^*_N - k^-_2 \theta^2_N \\
\frac{d\theta_{NH}}{dt} &= k^+_3 \theta_N \theta_H - k^-_3 \theta_{NH} \theta_* = 0 \Rightarrow \theta_N = \frac{\theta_{NH} \theta_*}{K_3 \theta_H} \\
\frac{d\theta_{NH_2}}{dt} &= k^+_4 \theta_{NH} \theta_H - k^-_4 \theta_{NH_2} \theta_* = 0 \Rightarrow \theta_{NH_2} = \frac{\theta_{NH} \theta_*}{K_4 \theta_H} \\
\frac{d\theta_{NH_3}}{dt} &= k^+_5 \theta_{NH_2} \theta_H - k^-_5 \theta_{NH_3} \theta_* = 0 \Rightarrow \theta_{NH_3} = \frac{\theta_{NH_2} \theta_*}{K_5 \theta_H} \\
\frac{d\theta_{NH_3}}{dt} &= -k^+_6 \theta_{NH_3} + k^-_6 p_{NH_3} \theta_* = 0 \Rightarrow \theta_{NH_3} = \frac{\theta_{NH_3} \theta_*}{K_6} \\
\frac{d\theta_H}{dt} &= k^+_7 p_{H_2} \theta^2_* - k^-_7 \theta^2_H = 0 \Rightarrow \theta_H = \sqrt{K_7 p_{H_2} \theta_*}
\end{align*}
\]

Microkinetic model

\[
\theta_* = \frac{1}{1 + K_1 p_{N_2} + \frac{p_{NH_3}}{K_3 K_4 K_5 K_6 (K_7 p_{H_2})^3} + \frac{p_{NH_3}}{K_4 K_5 K_6 K_7 p_{H_2}} + \frac{p_{NH_3}}{K_5 K_6 \sqrt{K_7 p_{H_2}}} + \frac{1}{K_6} p_{NH_3} + \sqrt{K_7 p_{H_2}}}
\]

\[
r = k_2^+ K_1 p_{N_2} \left( 1 - \frac{p_{NH_3}^2}{K_G p_{H_2}^3 p_{N_2}} \right) \theta_*^2
\]

\[
K_G = \frac{p_{NH_3}^2}{p_{H_2}^3 p_{N_2}} = K_1 K_2 K_3^2 K_4^2 K_5^2 K_6^2 K_7^3
\]

Fig. 1. Comparison of calculated and measured NH\textsubscript{3} mole fractions at the reactor outlet for the industrial catalyst Topsøe KM1R. The catalyst is operating at 1–300 atm, 375–500°C. The measurements at 150–300 atm are taken from Table I in Ref. (26). The 1-atm measurements are from Ref. (65).

Microkinetic model

Turn-over frequency calculated based on micro-kinetic modelling using parameters calculated by DFT

Structure and composition of the optimal catalyst is a function of the reaction condition

The role of potassium

Molecule and sp-band + d-band - The bottom line of surface reactivity

For molecules this may mean that the anti bonding orbitals get occupied resulting in bonding to the surface, but weakening of the internal bonding - the essence of catalysis.
The role of potassium

- Potassium as a promoter should have an influence on the rate-determining step
- The adsorption energy of molecularly adsorbed nitrogen is increased to 11.5 kcal/mol
- The work function of the model catalyst decreased
- This indicates electron transfer from potassium to iron
- This enables more pronounced back-donation from iron into the \( \pi^* \) orbital of nitrogen
- This weakens the N-N bond
Technology of ammonia synthesis

\[ \text{CH}_4 + 2 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 4 \text{H}_2 \]

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2 \]

\[ \text{CH}_4 + \text{air} \rightarrow \text{CO}_2 + \text{H}_2 + \text{N}_2 \]

\[ \text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3 \]

Ammonia plant (Haldor Topsøe AS) capable of producing totally 2x1350 tons ammonia per day over 2x150 tons catalyst.

Chorkendorff, p. 334.
Technology of ammonia synthesis

Process scheme (Haldor Topsøe AS) of ammonia synthesis

CH₄ + 2 H₂O ↔ Ni CO₂ + 4 H₂
CH₄ + H₂O ↔ CO + 3 H₂
CO + H₂O ↔ H₂ + CO₂ → washing
CO + 2 H₂ → CH₄ + H₂O

2 NO + O₂ → 2 NO₂
4 NH₃ + 5 O₂ → 4 NO + 6 H₂O

N₂ + 3 H₂ → Fe 2 NH₃

Chorkendorff, p. 334.
5.7. Determination of reaction mechanisms

- Models with predictive power exist for simple cases, like CO oxidation or ammonia synthesis.
- Selectivity is no issue in these reactions.
- Reaction in which selectivity matters are based on complex reaction networks.
- A general theory that is able to handle complexity is still missing.
- The dynamics of the catalyst are generally not included in kinetic considerations.