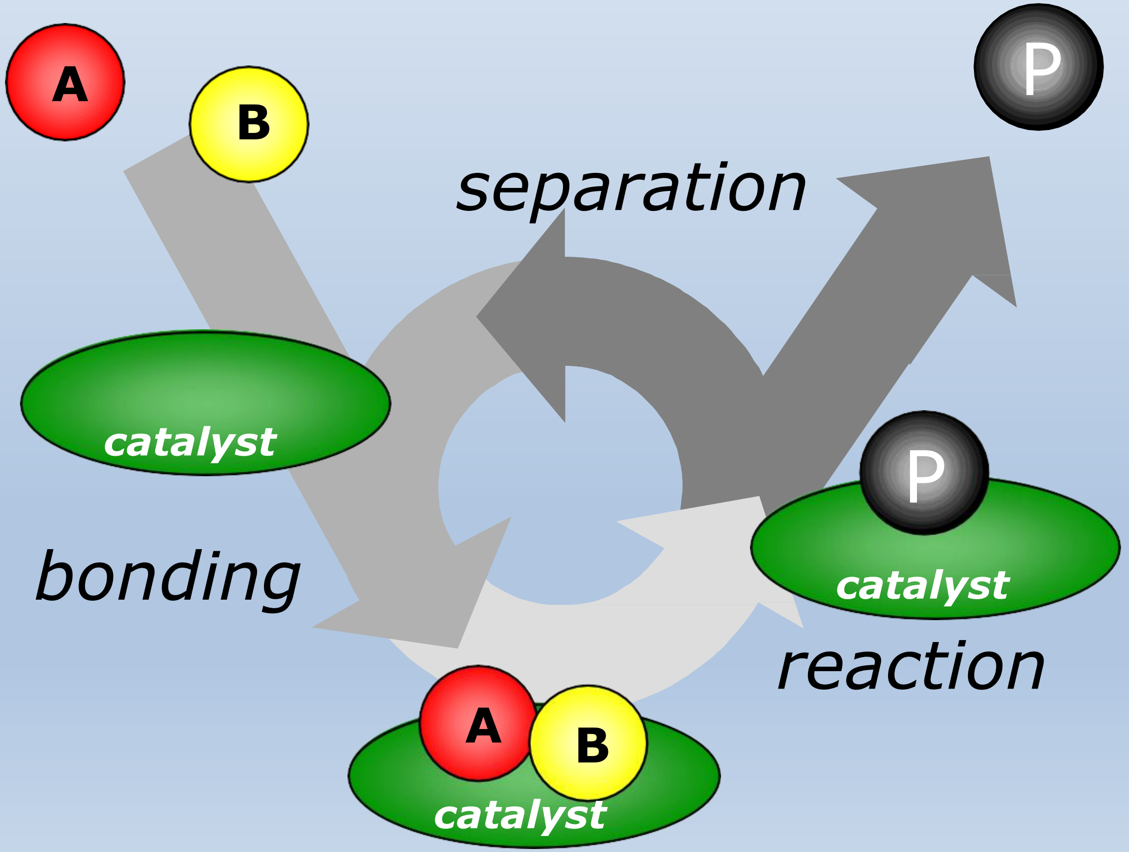
Heterogeneous Catalysis

Prof. Kamal M.S. Khalil

Chapter 1
Introduction

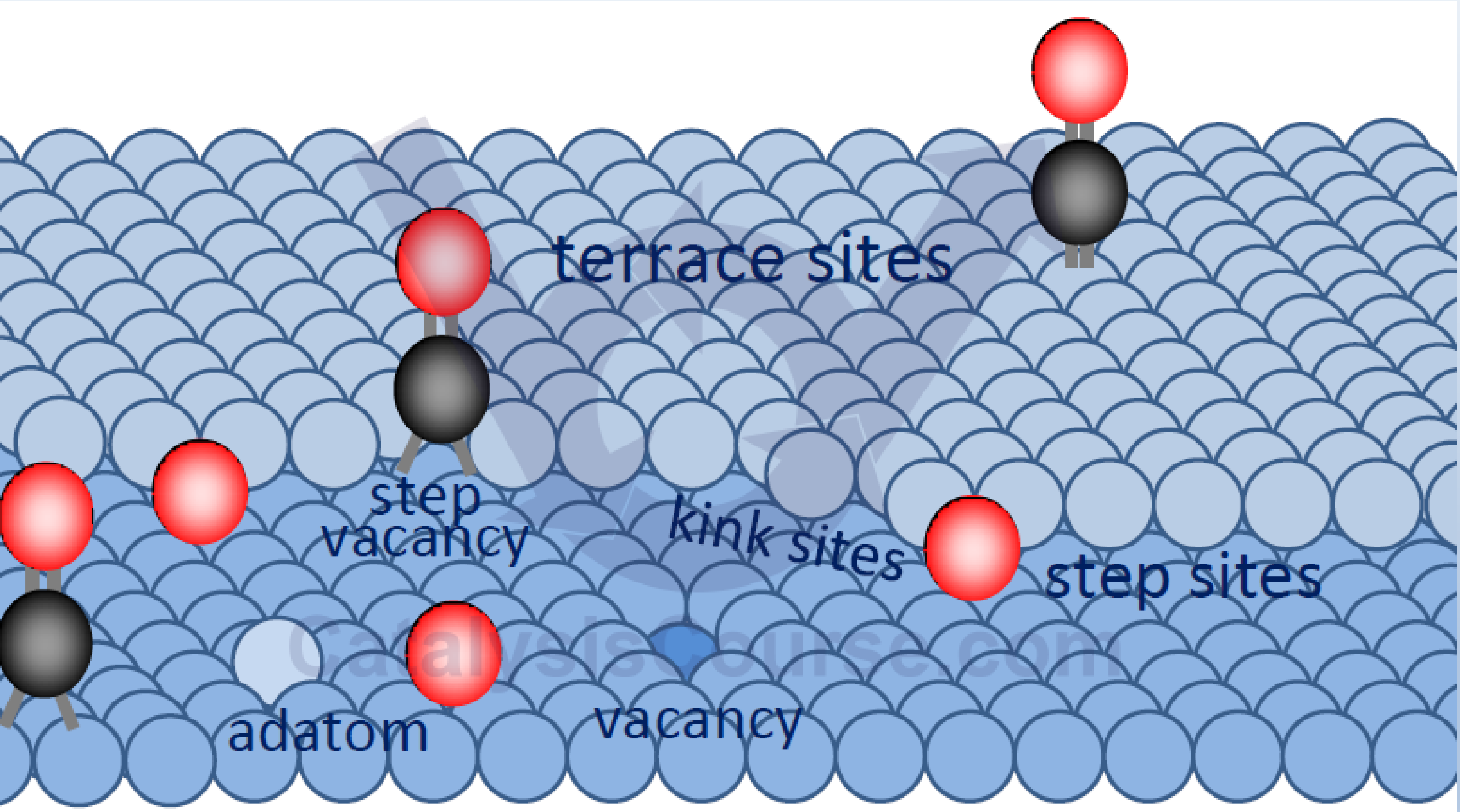
What is Catalysis?

a phenomenon in which a small quantity of a substance (the catalyst) increases the rate of a chemical reaction without being consumed

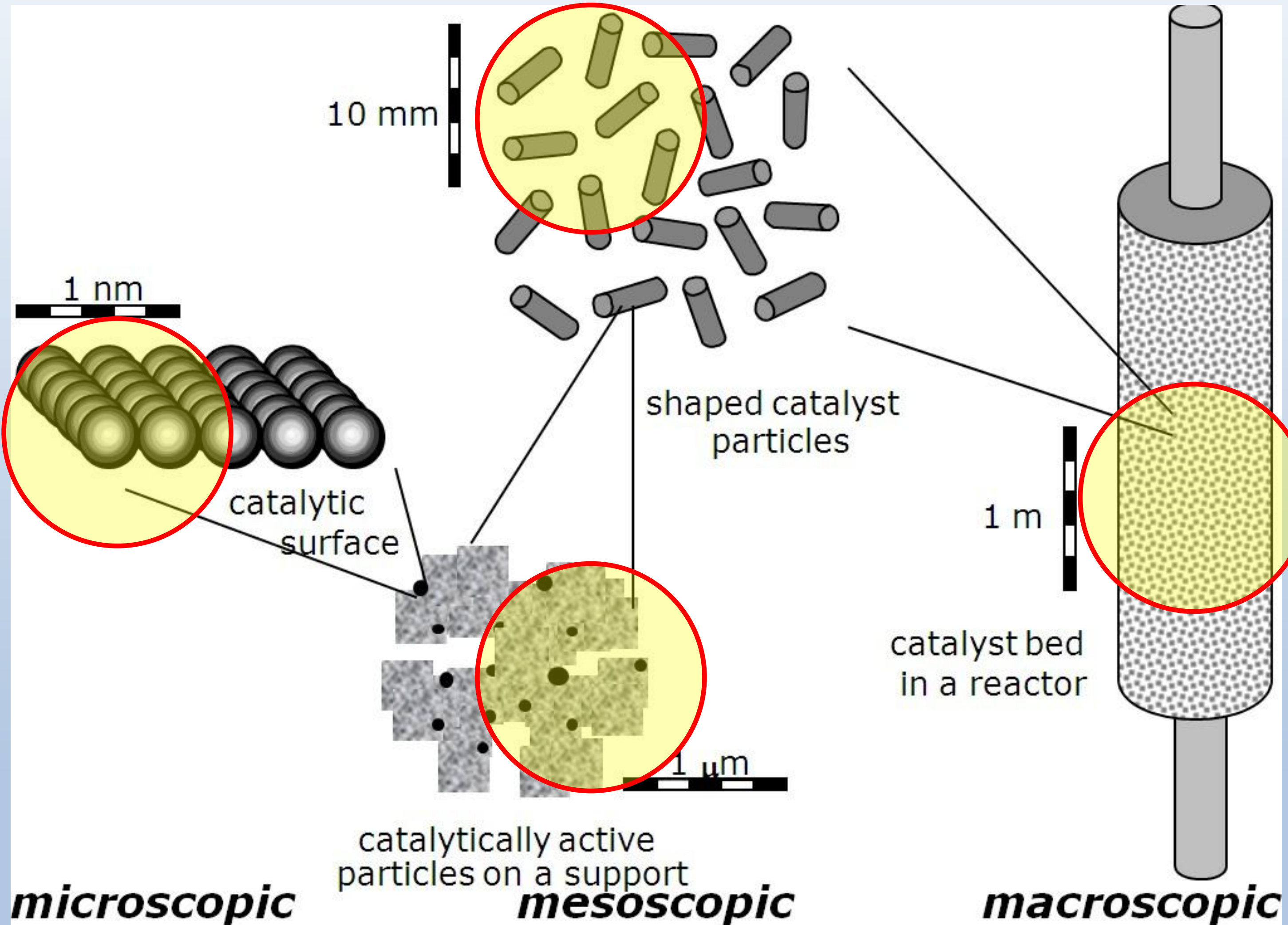


Catalysis is a cycle of elementary steps (at least three); catalytic sites are regenerated

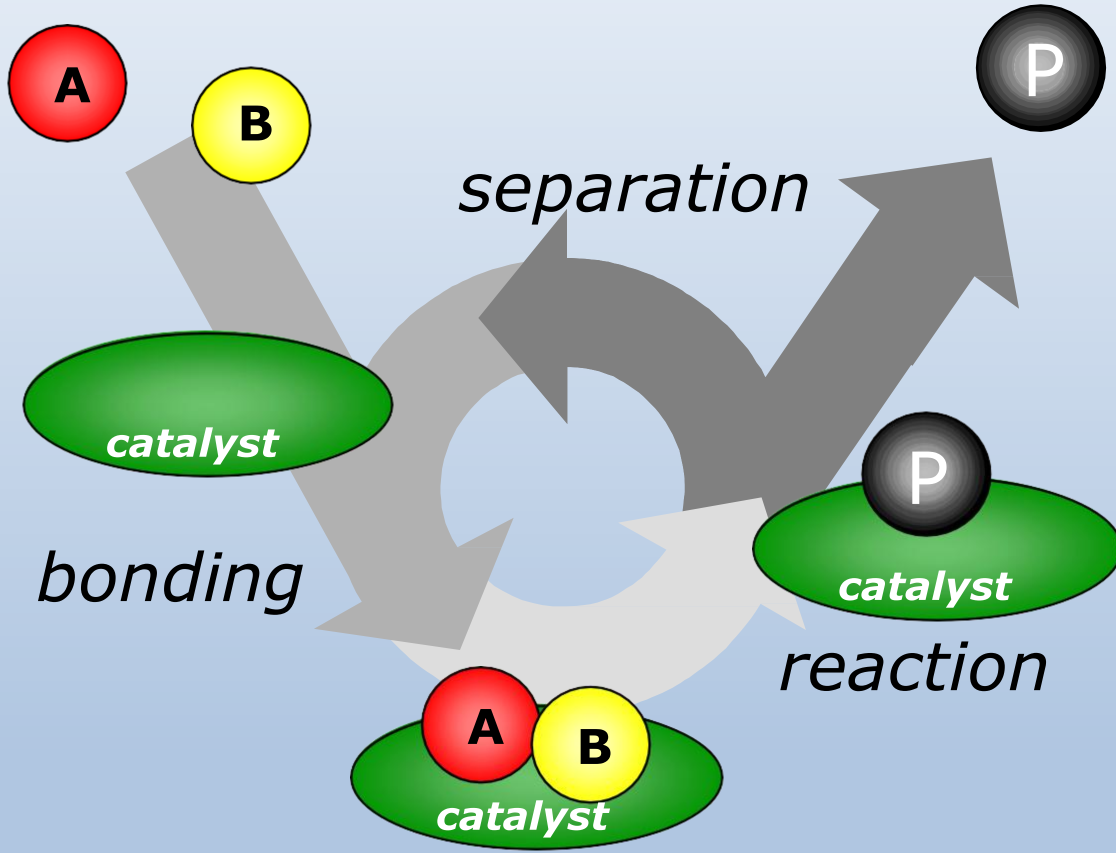
Catalyst is a complicated surface



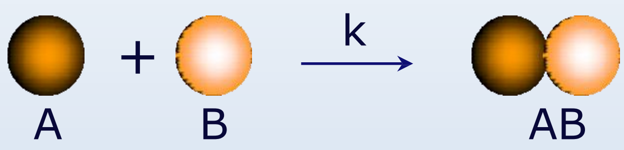
Multiple length and time scales



Catalysis is a cycle…

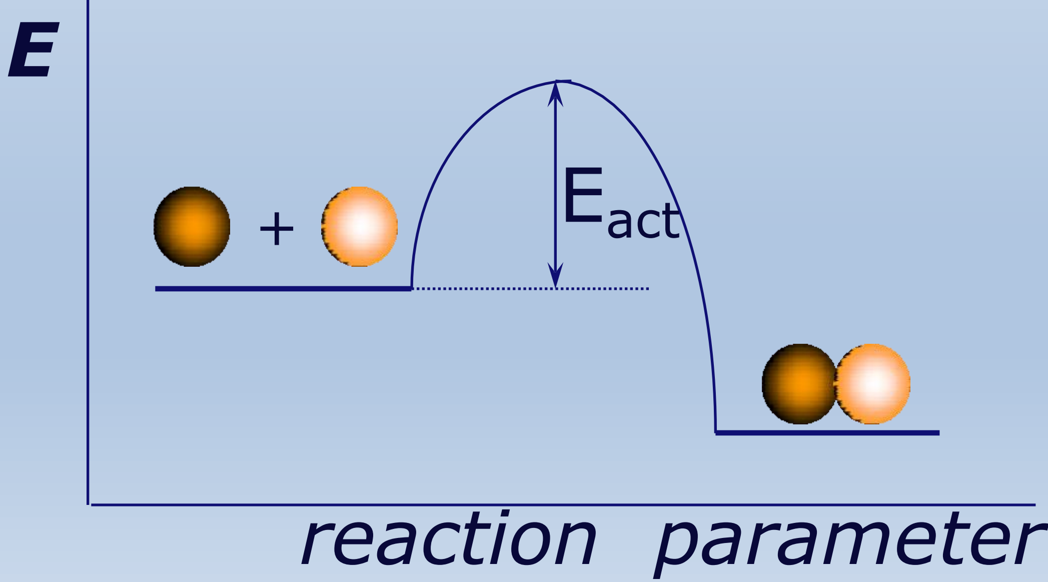


The Arrhenius Equation



$$r = \frac{d[AB]}{dt} = k\,[A][B]$$

$$k = \nu\, e^{-E_{act}/RT}$$

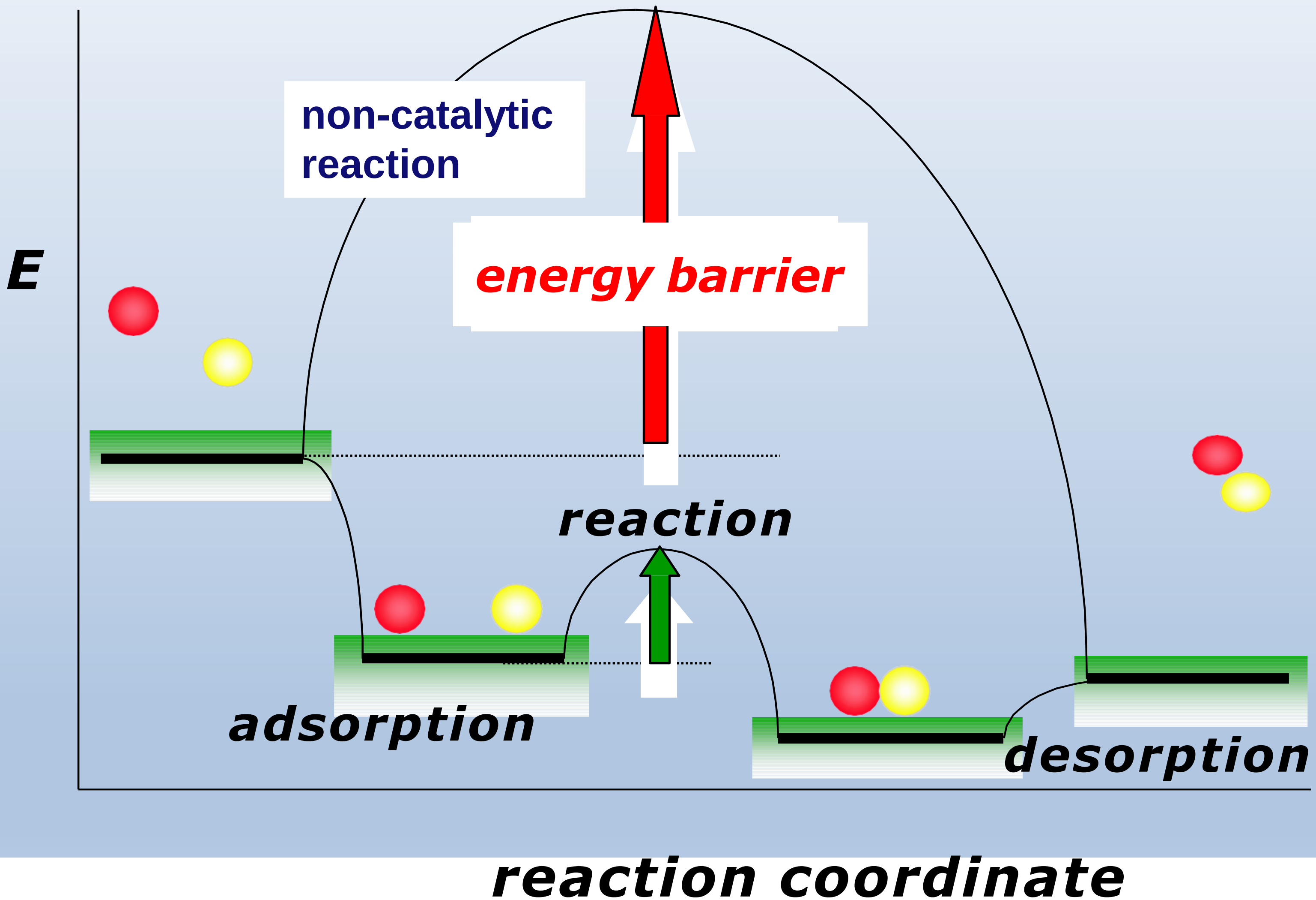


Svante Arrhenius

1859 - 1927

Nobel Prize 1903

Energy profile of a catalytic reaction



Energy barrier of the catalytic route is much lower.

The energy diagram illustrates :

1. The catalyst offers an alternative reaction path, which is more complex, but energetically much more favorable.
2. The activation energy of the catalytic reaction is smaller than that of the uncatalyzed reaction; hence, the rate of the catalytic reaction is much higher.
3. The overall change in free energy for the catalytic reaction equals that of the uncatalyzed reaction. Hence, the catalyst does not affect the equilibrium constant for the overall reaction of A + B to P.
4. Thus, if a reaction is thermodynamically unfavorable, a catalyst cannot change this situation.
5. A catalyst changes the kinetics but not the thermodynamics of the reaction.

Cases in which the catalyst will not be successful with reactants

1. **If the bonding between reactants and catalyst is too weak, there will not be any conversion into products.**
2. **If the bond between the catalyst and one of the reactants, say A, is too strong, the catalyst will be occupied with A, and no space for B to interact.**
3. **If A and B both form strong bonds with the catalyst, the intermediate situation with A or B on the catalyst may be so stable that reaction becomes unlikely.**
4. **In terms of Fig. 1.2, the second level lies so deep that the activation energy to form P on the catalyst becomes too high. The catalyst is poisoned by the reactant(s).**
5. **If the product P too strongly bound to the catalyst this prevent separation to occur. The catalyst is poisoned by the product.**

Catalysts forms, mediums, preparation and characterization

Catalyst Forms Catalysts come in a multitude of forms

- atoms and molecules, and in large structures such as zeolites or enzymes.

Catalyst mediums Catalysts may be employed in various mediums

- in liquids, gases or at the surface of solids.

Preparation Characterization Preparation of a catalyst in the optimum form

- Studying its precise composition and shape are an important specialism

The sub disciplines in catalysis:

There are three sub disciplines in catalysis:

- Homogeneous
- Heterogeneous
- Bio catalysis.

Homogeneous Catalysis

In homogeneous catalysis, both the catalyst and the reactants are in the same phase

i.e. all are molecules in the gas phase, or, more commonly, in the liquid phase.

Example: Ozone in the atmosphere decomposes, among other routes, via a reaction with chlorine atoms:

$$Cl + O_3 \longrightarrow ClO_3$$

$$ClO_3 \longrightarrow ClO + O_2$$

$$ClO + O \longrightarrow Cl + O_2$$

or overall

$$O_3 + O \longrightarrow 2O_2$$

O_3 can decompose spontaneously, and also under the influence of light, but a Cl atom accelerates the reaction tremendously.

Heterogeneous Catalysis

- In heterogeneous catalysis, solids catalyze reactions of molecules in gas or solution.
- For nonporous solid catalysts, catalytic reactions occur at the surface.
- To use the often expensive materials (e.g. platinum) in an economical way, catalysts are usually nanometer-sized particles, supported on an inert, porous structure (see Fig. 1.4).
- Heterogeneous catalysts are the workhorses of the chemical and petrochemical industry.
- Heterogeneous catalysts and many of their applications will be discuss throughout this course.

Catalysis : Nanomaterials and nanotechnology

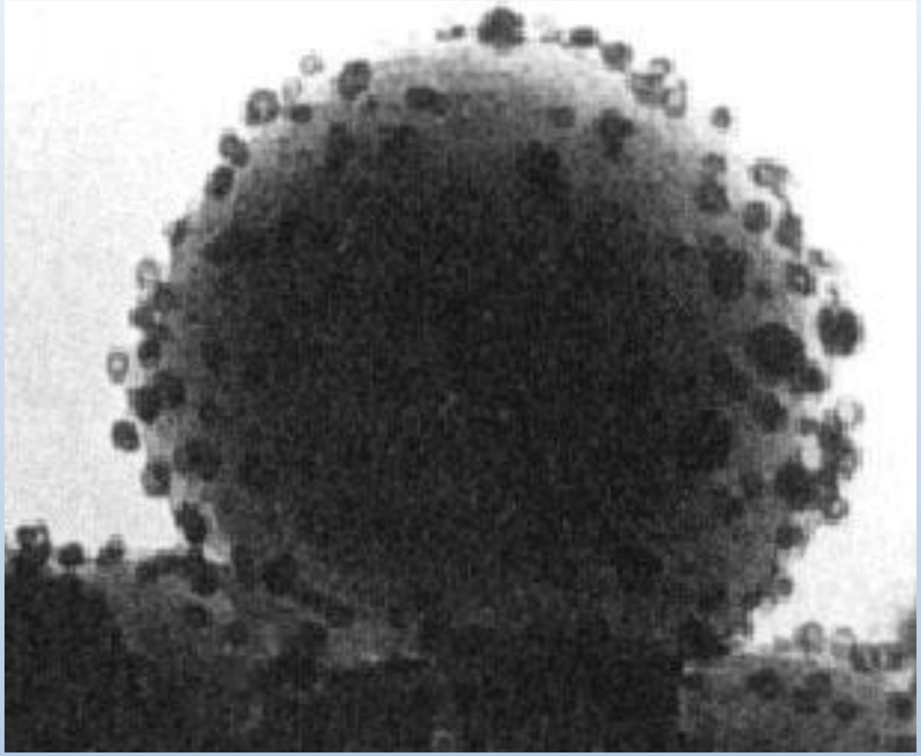


Figure 1.4. Catalysts are nanomaterials and catalysis is nanotechnology.

Catalysis represents a field where nanomaterials have been applied.

Modern catalysis is principally nanotechnology

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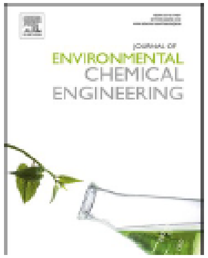

Biomass derived P-containing activated carbon as a novel green catalyst/ support for methanol conversion to dimethyl ether alternative fuel

Kamal M.S. Khalil [a,*], Walaa A. Elhamdy [a], Mohamed N. Goda [b], Abd El-Aziz A. Said [b]

[a] *Chemistry Department, Faculty of Science, Sohag University, P.O. Box 82524, Sohag, Egypt*
[b] *Chemistry Department, Faculty of Science, Assiut University, P.O. Box 71516, Assiut, Egypt*

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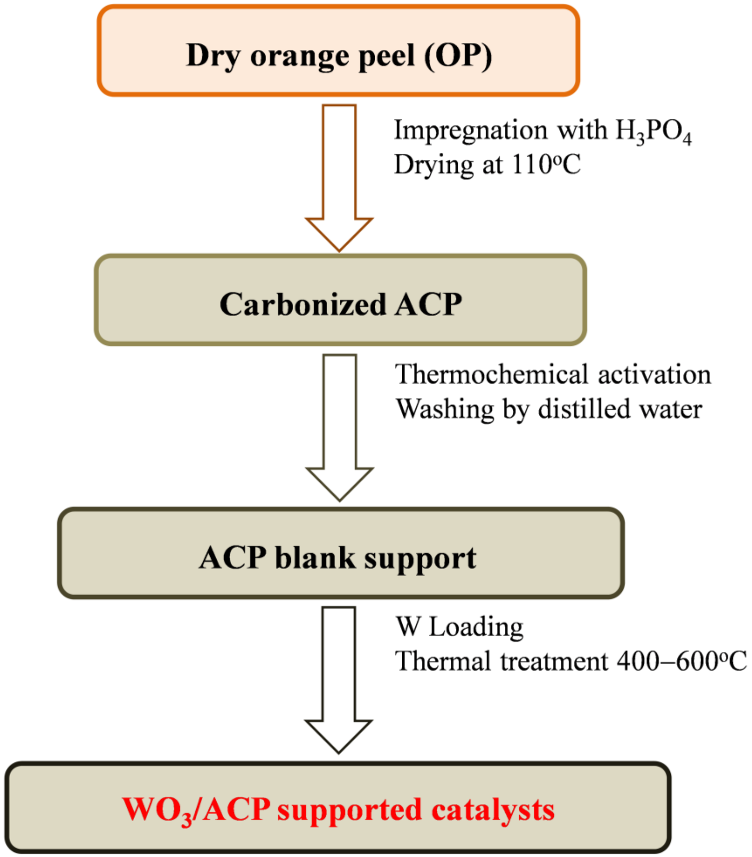
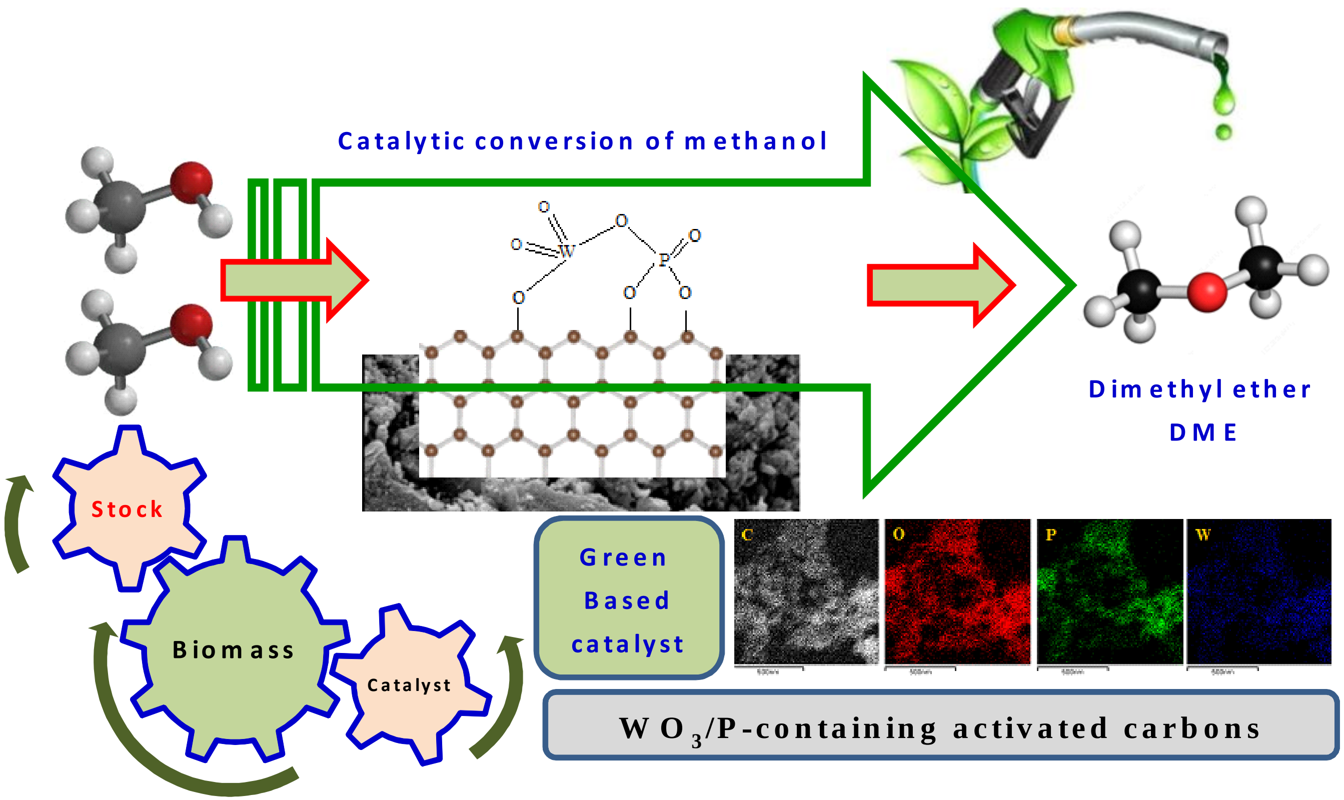
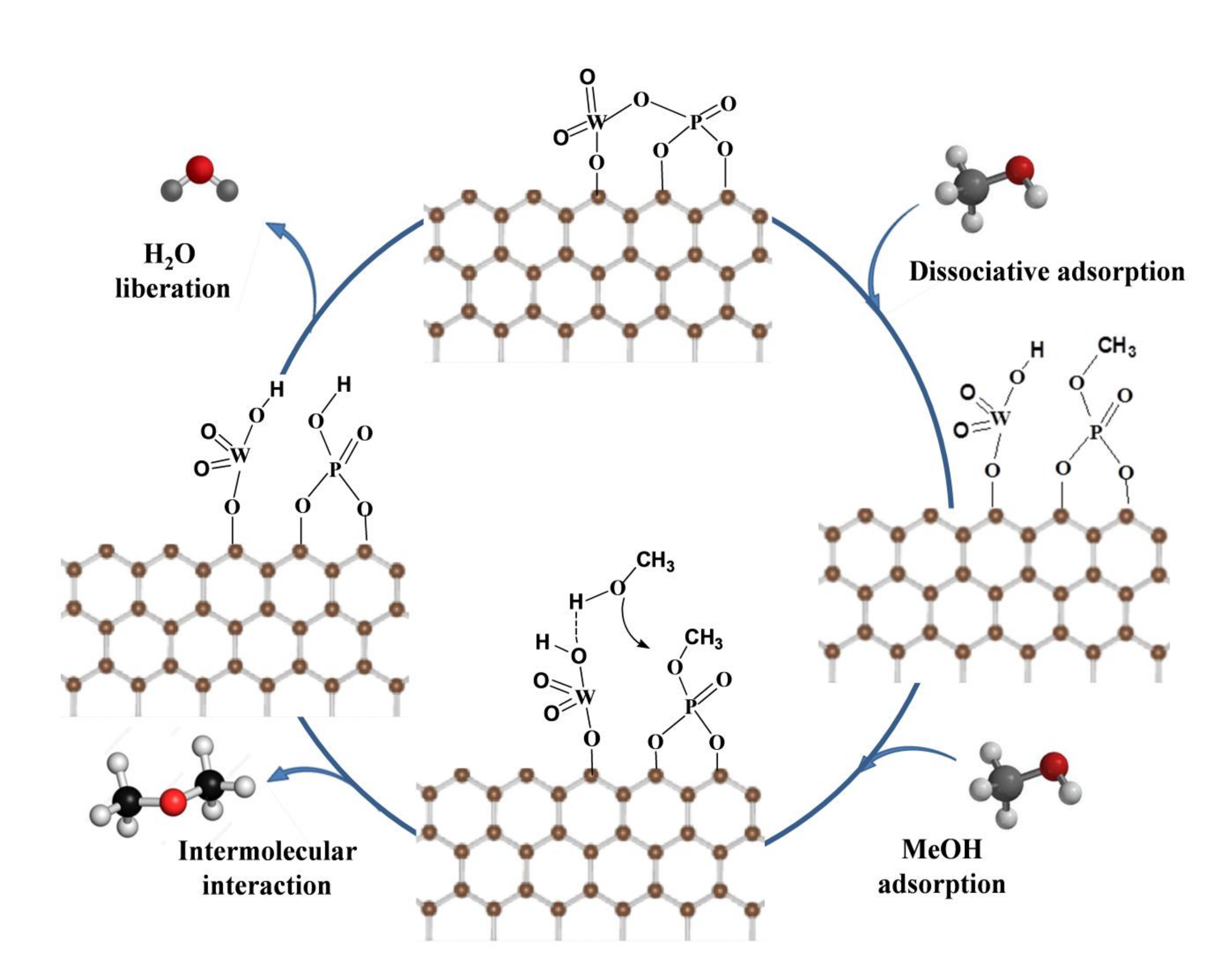
ABSTRACT

The current environmental situation has urged researchers to look for alternative green fuels with lower emissions from biomass feedstock. This work aims a greener approach for the heterogeneous catalytic conversion of methanol to dimethyl ether, DME, as an alternative fuel. Thus, a series of phosphorous–containing activated


Dry orange peel (OP)
Impregnation with H_3PO_4
Drying at 110°C
Carbonized ACP
Thermochemical activation
Washing by distilled water
ACP blank support
W Loading
Thermal treatment 400–600°C
WO_3/ACP supported catalysts

Biomass derived P-containing activated carbons as a novel green catalyst/support for methanol conversion to dimethyl ether alternative fuel





H2O
liberation
Dissociative adsorption
MeOH
adsorption
Intermolecular
interaction

The catalytic oxidation of CO

on the surface of noble metals

such as platinum, palladium and rhodium

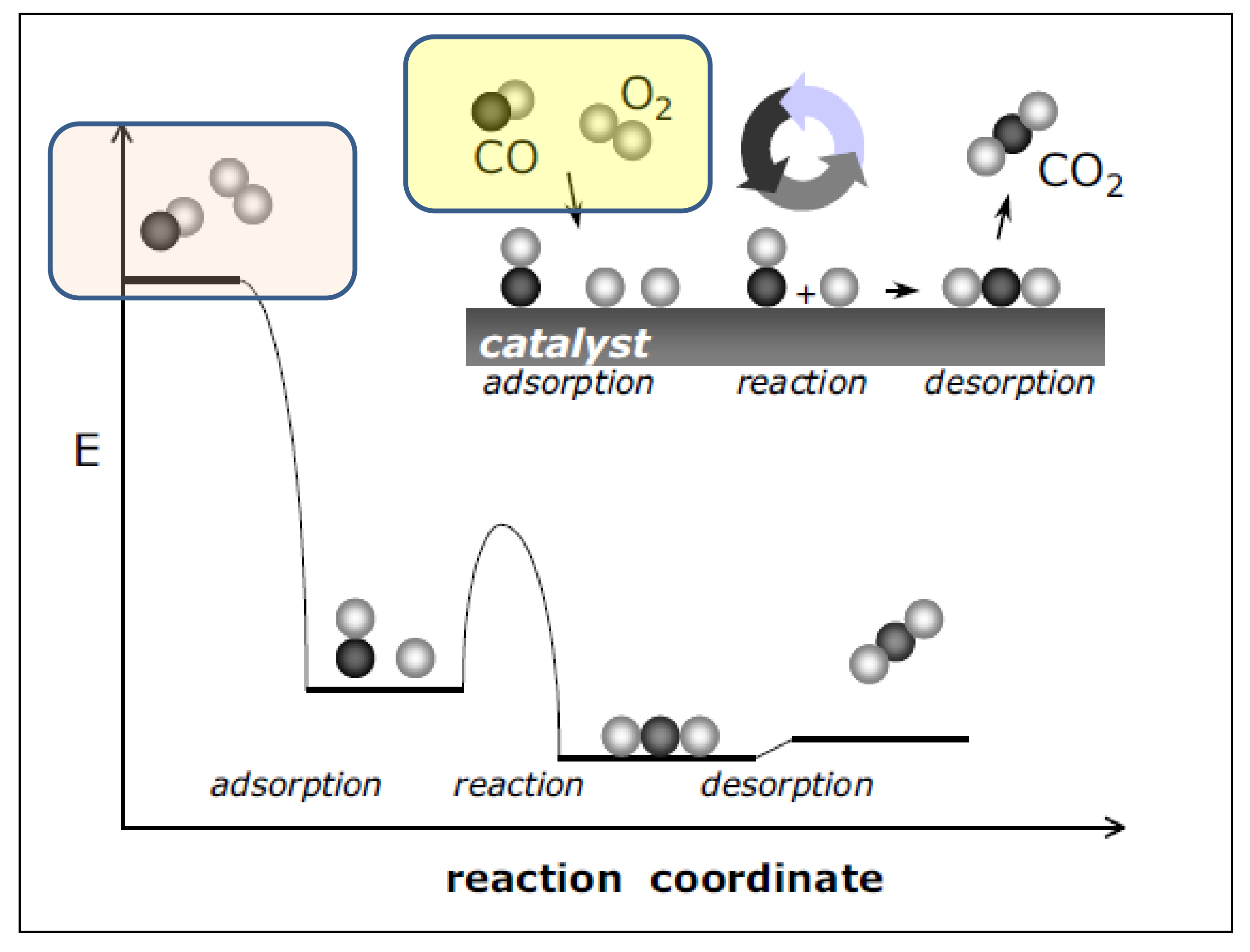


Figure 1.5.

The catalytic oxidation of CO

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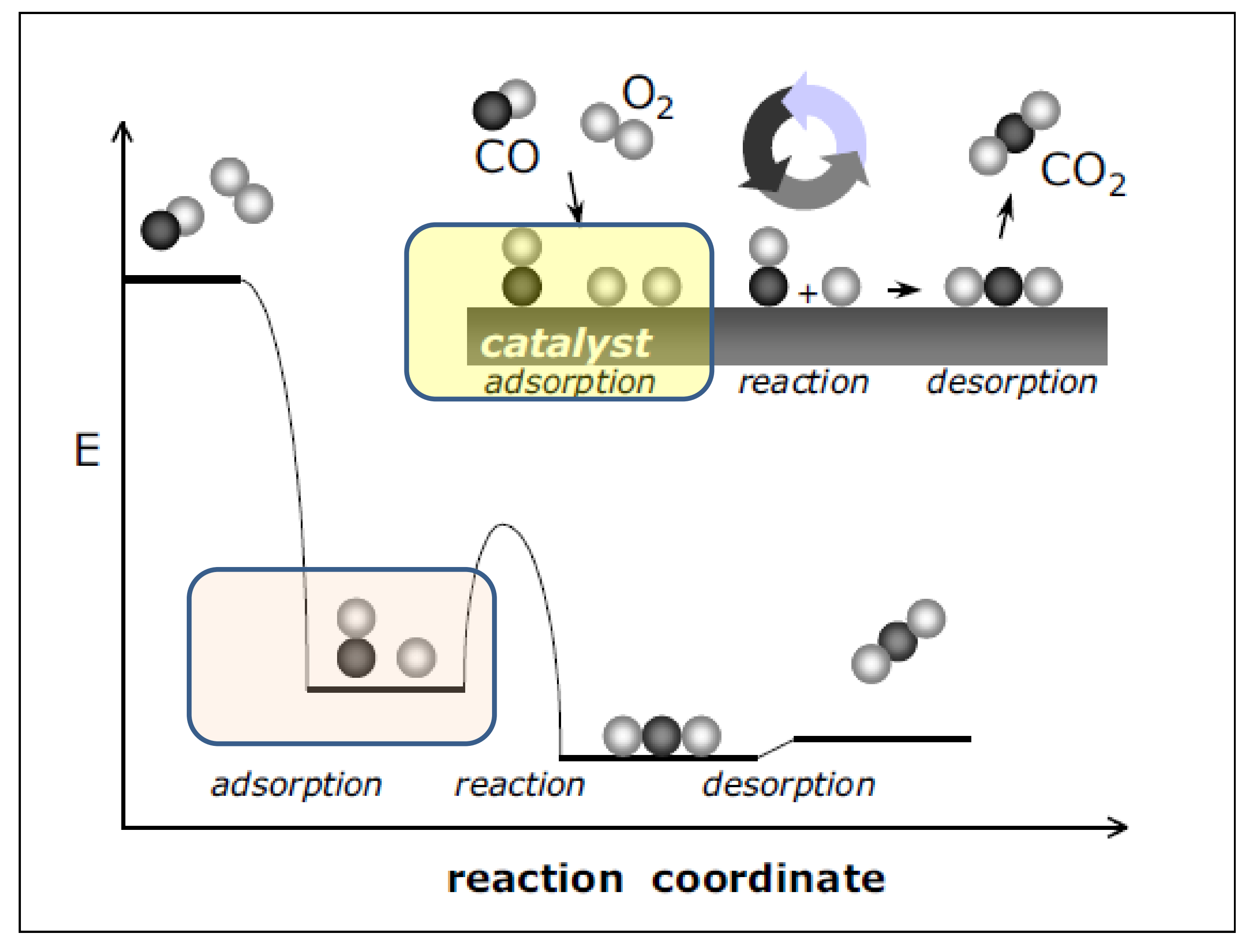

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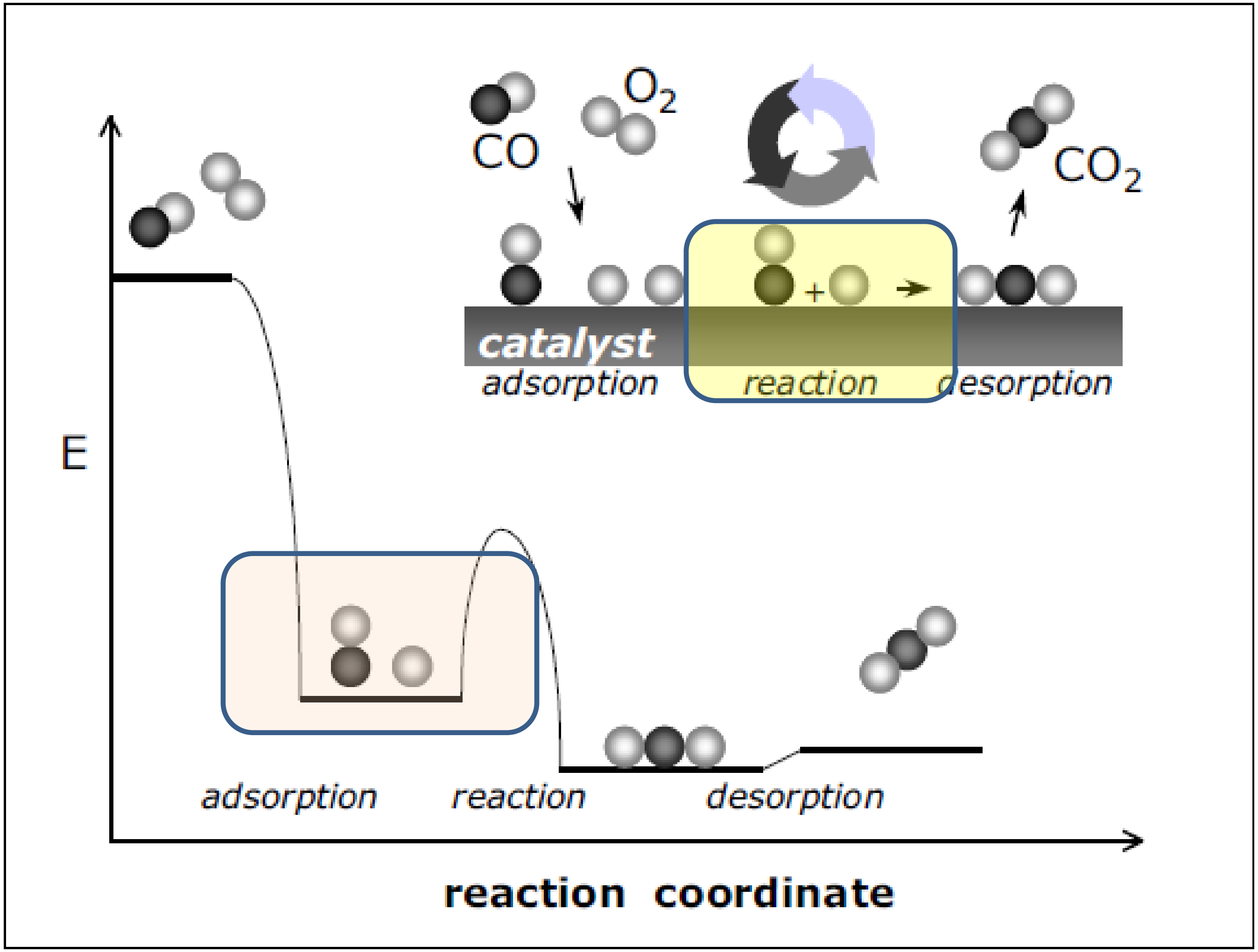

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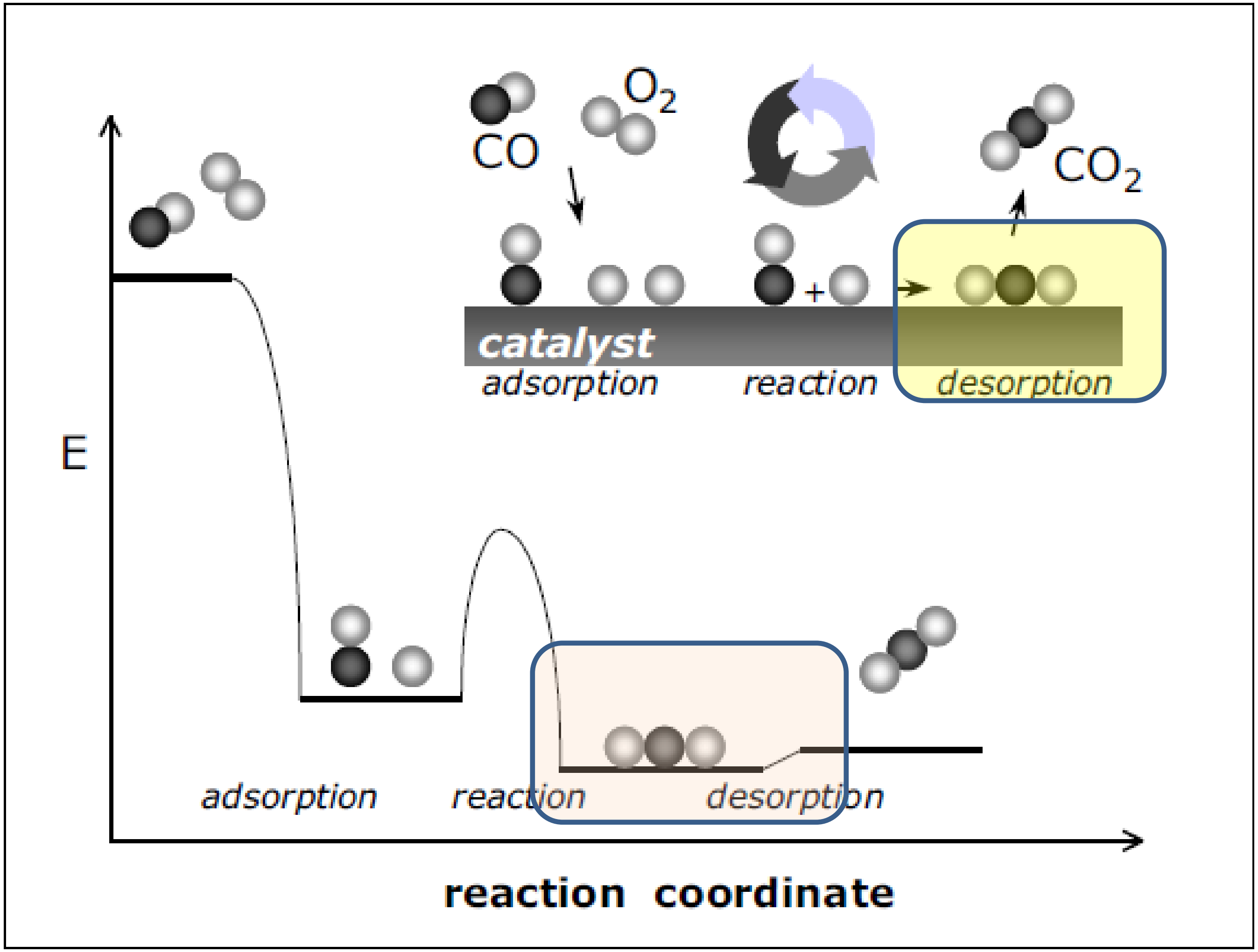

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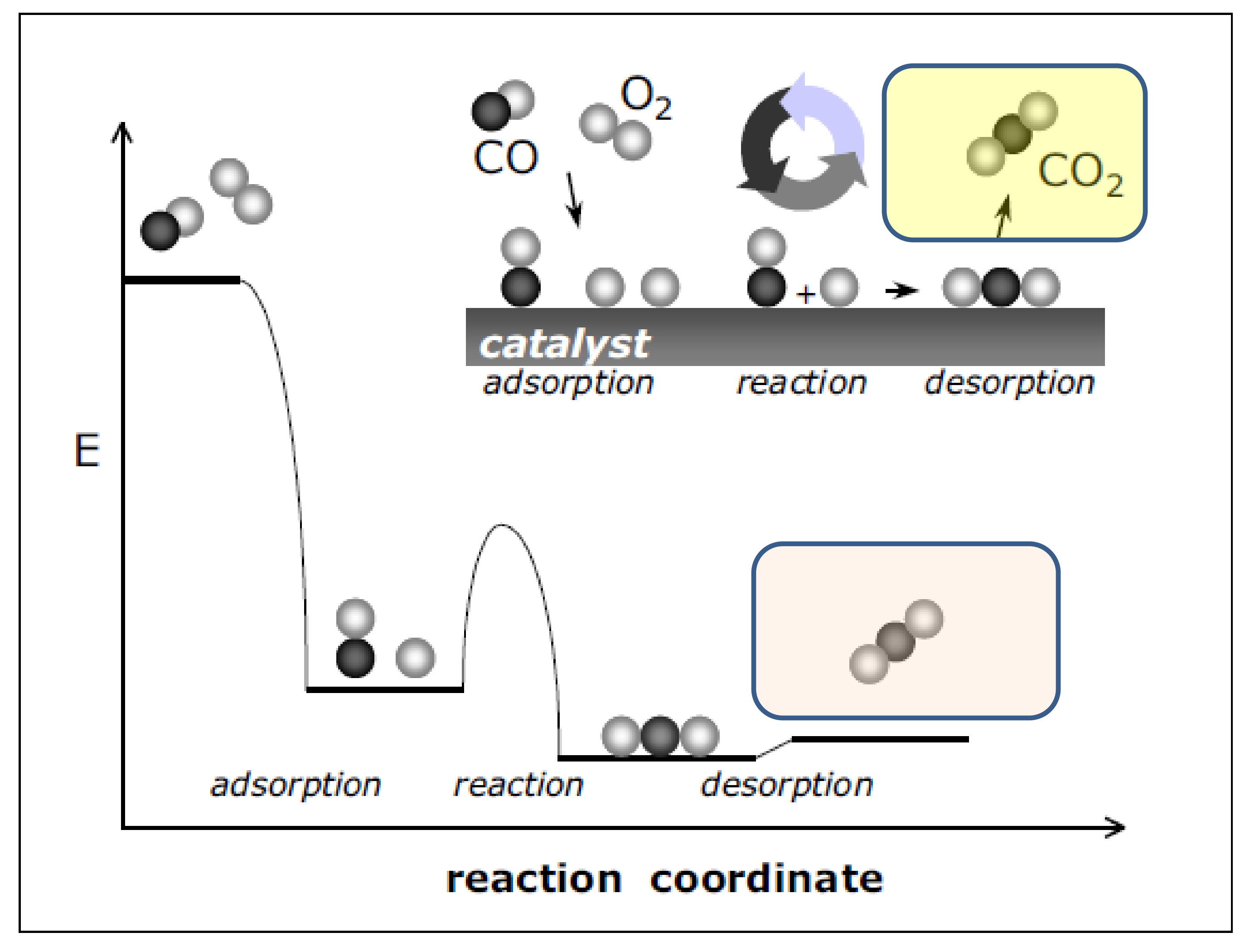


Figure 1.5.

$$O_2 + 2^* \rightleftharpoons 2O^*$$
$$CO + ^* \rightleftharpoons CO^*$$

The adsorbed O atom and the adsorbed CO molecule react on the surface to form CO2, which, being very stable and relatively unreactive, interacts only weakly with the platinum surface and desorbs almost instantaneously

$$CO^* + O^* \rightleftarrows CO_2 + 2^*$$

The Arrhenius Equation

$$k = \nu e^{-E_{act}/RT}$$

Activation energy lower:

Reaction temperature lower!!

Example: Suppose

reaction without catalyst: E_{act} **= 250 kJ/mol**
then $T_{reaction}$ **≈ 1000 K**

however, if with a catalyst E_{act} **= 100 kJ/mol**
then $T_{reaction}$ **≈ 400 K !!!**

Ammonia Synthesis

$$N_2 + 3\,H_2 = 2\,NH_3 + \text{heat}$$

equilibrium reaction !

What are favorable conditions?

- **pressure:** **high**
- **temperature:** **low**
- **kinetics slow:** **catalyst !!**

Ammonia Synthesis

Source of nitrogen:

air

Source of hydrogen:

natural gas and water

Steam Reforming: Ni on a support

$$CH_4 + H_2O = CO + H_2$$

Water Gas Shift: More H_2

Low Temperature : $Cu + ZnO + Al_2O_3$

High-temperature: Fe_3O_4

$$CO + H_2O = CO_2 + H_2$$

Ammonia Synthesis:

$Fe_3O_4 + K + Al_2O_3$

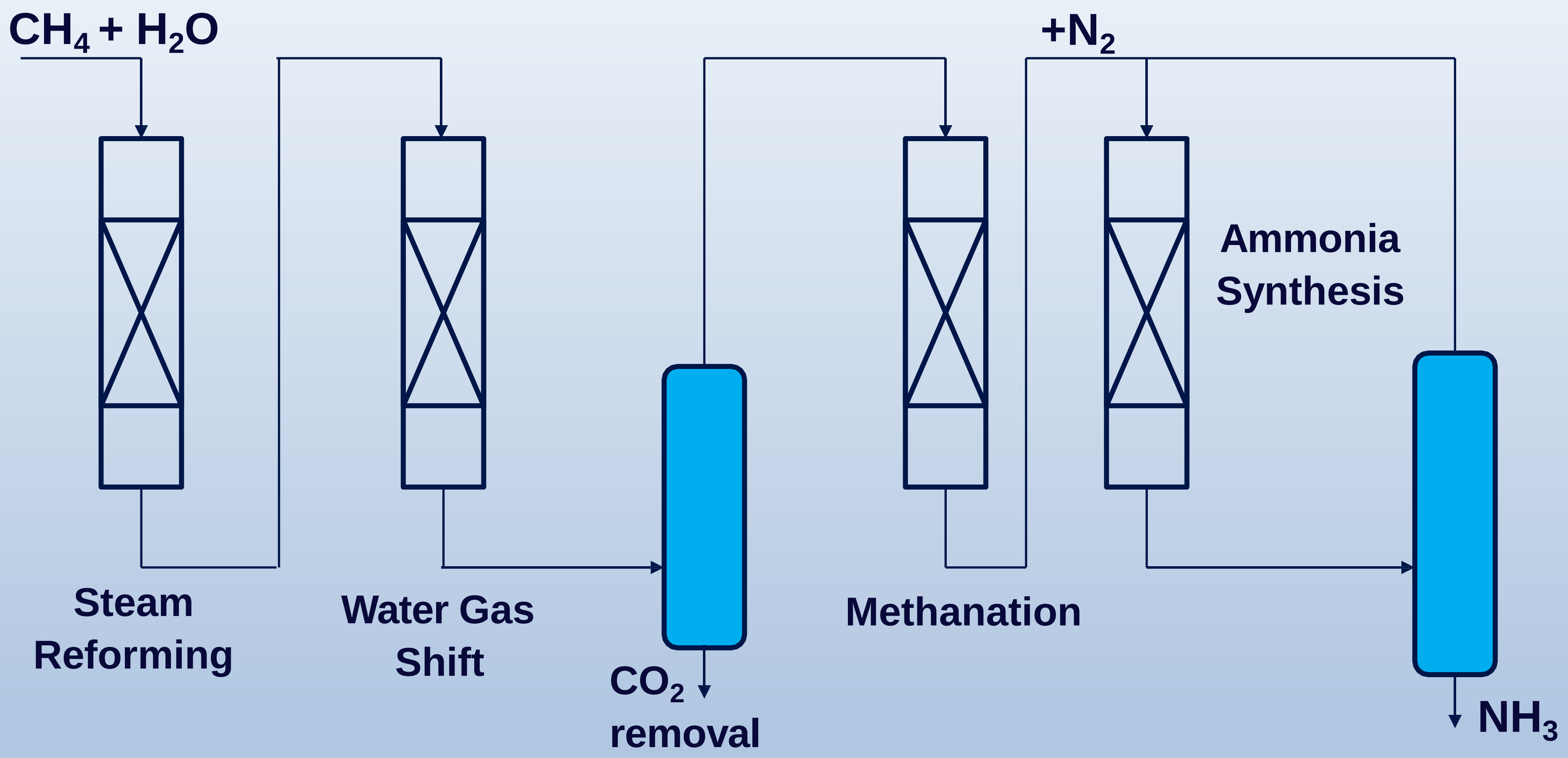
$$N_2 + 3H_2 = 2NH_3$$

What is the essential action of the catalyst?

Why iron?

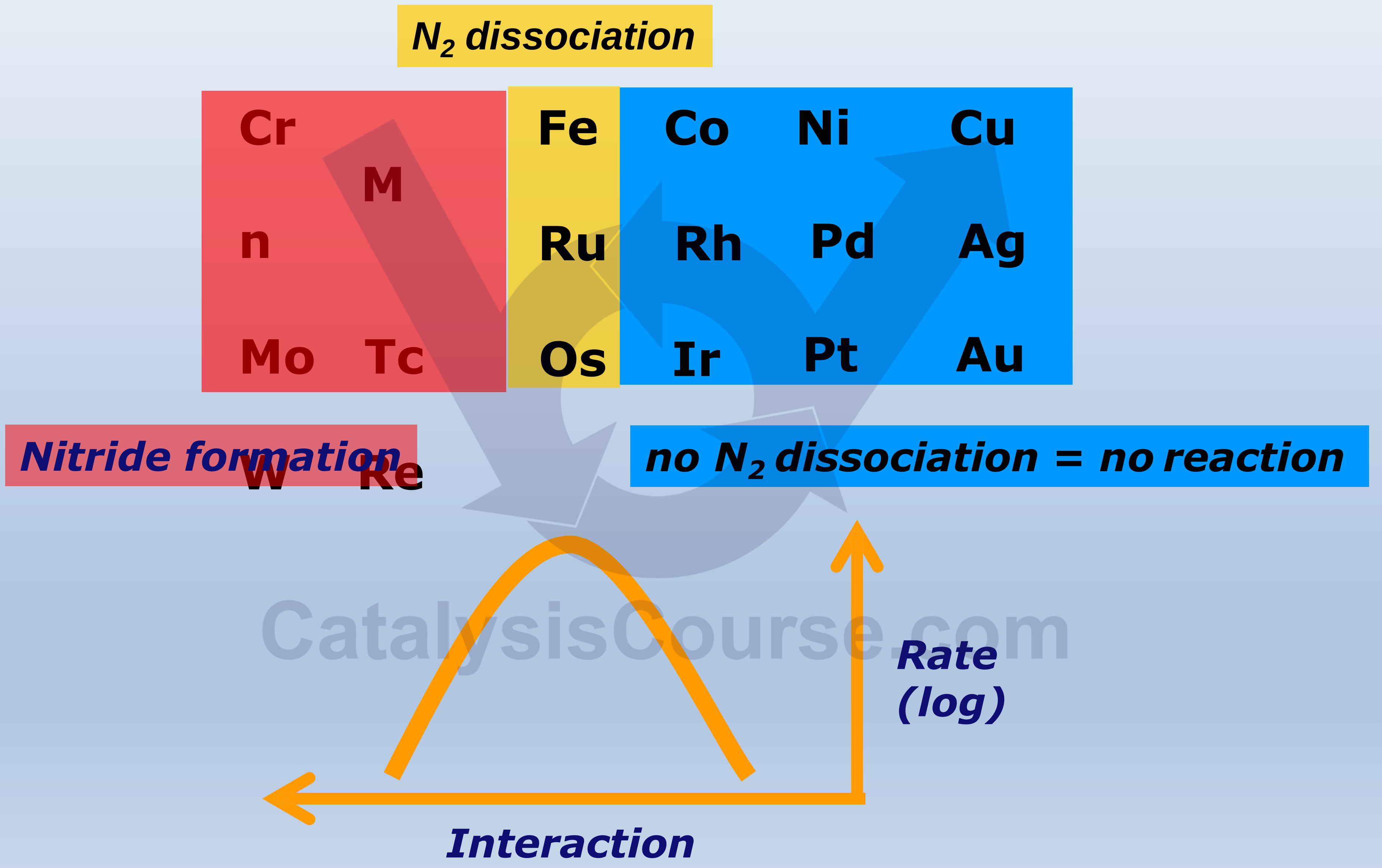
Courtesy Haldor Topsoe

Ammonia Synthesis



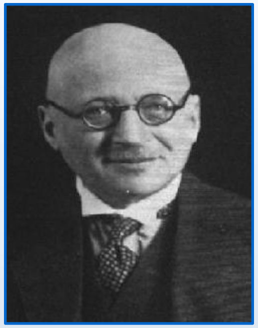
5 catalytic processes!

Metal Catalysts in NH_3 Synthesis

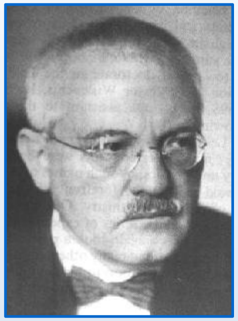


Ammonia Synthesis

(1908 - 1913)



Haber



Bosch

Mittasch

- **conditions understood in early 20th century**
- **screening of 2500 catalysts in 6000 tests**
- **1913: plant opened at Oppau - Ludwigshafen**
- **produced ammonium sulfate (fertilizer)**
- **1914 redesigned to produce nitrate**

Development of ammonia synthesis:

- **start of chemical engineering**
- **high pressure reaction technology**
- **stimulus for catalysis**

Catalysts

- increase the rate of a reaction
- without being consumed in the process

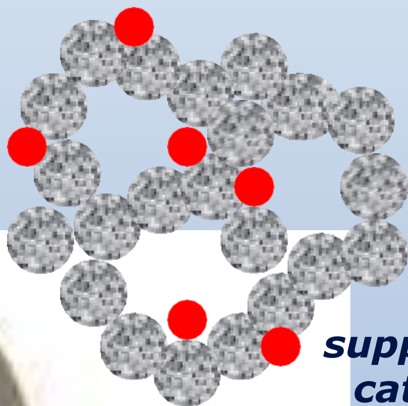
✓offer alternative, energetically favorable pathways for reactions

✓ enable reactions to occur under industrially achievable conditions

✓allow selective production routes without or with less undesirable byproducts

✓ are the work horses of the chemical industry

✓ are the key enablers for sustainable (green)production



supported catalyst

catalyst pellets and extrudates

Courtesy Haldor Topsoe