Kinetika Kimia

Studi/kajian tentang laju reaksi

http:// fpmipa.upi.edu/kuliahonline

- Pengertian Laju reaksi
- Pengukuran Laju
- Penentuan Hk. Laju
- Pengaruh Temperatur pada Laju reaksi
- Mechanisme Reaksi
- Catalysis

Catalysis & Catalysts

- Facts and Figures about Catalysts

Life cycle on the earth

› Catalysts (enzyme) participates most part of life cycle

e.g. forming, growing, decaying

› Catalysis contributes great part in the processes of converting sun energy to various other forms of energies

e.g. photosynthesis by plant $CO_2 + H_2O = HC + O_2$

› Catalysis plays a key role in maintaining our environment

Chemical Industry

› ca. $2 bn annual sale of catalysts

› ca. $200 bn annual sale of the chemicals that are related products

› 90% of chemical industry has catalysis-related processes

› Catalysts contributes ca. 2% of total investment in a chemical process

What is Catalysis

- Catalysis
  - Catalysis is an action by catalyst which takes part in a chemical reaction process and can alter the rate of reactions, and yet itself will return to its original form without being consumed or destroyed at the end of the reactions

    (This is one of many definitions)

Three key aspects of catalyst action

- taking part in the reaction
  - it will change itself during the process by interacting with other reactant/product molecules
- altering the rates of reactions
  - in most cases the rates of reactions are increased by the action of catalysts; however, in some situations the rates of undesired reactions are selectively suppressed
- Returning to its original form
  - After reaction cycles a catalyst with exactly the same nature is ‘reborn’
  - In practice a catalyst has its lifespan - it deactivates gradually during use

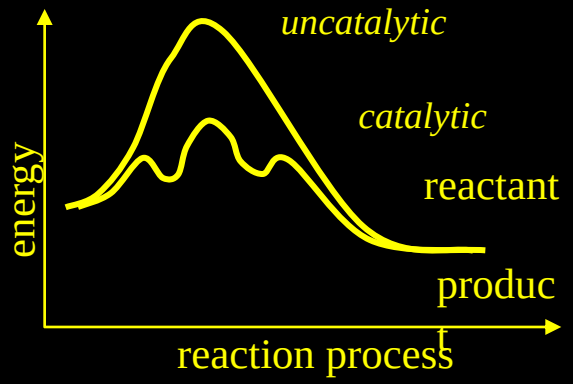
Action of Catalysts

- Catalysis action - Reaction kinetics and mechanism

  Catalyst action leads to the rate of a reaction to change.

  This is realised by changing the course of reaction (compared to non-catalytic reaction)

  - Forming complex with reactants/products, controlling the rate of elementary steps in the process. This is evidenced by the facts that
    - The reaction activation energy is altered
    - The intermediates formed are different from those formed in non-catalytic reaction
    - The rates of reactions are altered (both desired and undesired ones)



  - Reactions proceed under less demanding conditions
    - Allow reactions occur under a milder conditions, e.g. at lower temperatures for those heat sensitive materials

Action of Catalysts

- It is important to remember that the use of catalyst DOES NOT vary ΔG & K_{eq} values of the reaction concerned, it merely change the PACE of the process
  - Whether a reaction can proceed or not and to what extent a reaction can proceed is solely determined by the reaction thermodynamics, which is governed by the values of ΔG & K_{eq}, NOT by the presence of catalysts.
  - In another word, the reaction thermodynamics provide the driving force for a rxn; the presence of catalysts changes the way how driving force acts on that process.

e.g $CH_4(g) + CO_2(g) = 2CO(g) + 2H_2(g)$

$\Delta G°_{373}$=151 kJ/mol (100 °C)

$\Delta G°_{973}$ =-16 kJ/mol (700 °C)

- At 100°C, $\Delta G°_{373}$=151 kJ/mol > 0. There is no thermodynamic driving force, the reaction won't proceed with or without a catalyst
- At 700°C, $\Delta G°_{373}$= -16 kJ/mol < 0. The thermodynamic driving force is there. However, simply putting CH_4 and CO_2 together in a reactor does not mean they will react. Without a proper catalyst heating the mixture in reactor results no conversion of CH_4 and CO_2 at all. When Pt/ZrO_2 or Ni/Al_2O_3 is present in the reactor at the same temperature, equilibrium conversion can be achieved (<100%).

Types of Catalysts & Catalytic Reactions

- The types of catalysts
  - Classification based on the its physical state, a catalyst can be
    - gas
    - liquid
    - solid
  - Classification based on the substances from which a catalyst is made
    - Inorganic (gases, metals, metal oxides, inorganic acids, bases etc.)
    - Organic (organic acids, enzymes etc.)
  - Classification based on the ways catalysts work
    - Homogeneous - both catalyst and all reactants/products are in the same phase (gas or liq)
    - Heterogeneous - reaction system involves multi-phase (catalysts + reactants/products)
  - Classification based on the catalysts' action
    - Acid-base catalysts
    - Enzymatic
    - Photocatalysis
    - Electrocatalysis, etc.

Applications of Catalysis

- Industrial applications

  Almost all chemical industries have one or more steps employing catalysts

  › Petroleum, energy sector, fertiliser, pharmaceutical, fine chemicals …

  Advantages of catalytic processes

  › Achieving better process economics and productivity
    - Increase reaction rates - fast
    - Simplify the reaction steps - low investment cost
    - Carry out reaction under mild conditions (e.g. low T, P) - low energy consumption

  › Reducing wastes
    - Improving selectivity toward desired products - less raw materials required, less unwanted wastes
    - Replacing harmful/toxic materials with readily available ones

  › Producing certain products that may not be possible without catalysts

  › Having better control of process (safety, flexible etc.)

  › Encouraging application and advancement of new technologies and materials

  › And many more …

Applications of Catalysis

- Environmental applications
  - Pollution controls in combination with industrial processes
    - Pre-treatment - reduce the amount waste/change the composition of emissions
    - Post-treatments - once formed, reduce and convert emissions
    - Using alternative materials
    - …
  - Pollution reduction
    - gas - converting harmful gases to non-harmful ones
    - liquid - de-pollution, de-odder, de-colour etc
    - solid - landfill, factory wastes
    - …
  - And many more …

- Other applications
  - Catalysis and catalysts play one of the key roles in new technology development.

Research in Catalysis

- Research in catalysis involve a multi-discipline approach
  - Reaction kinetics and mechanism
    - Reaction paths, intermediate formation & action, interpretation of results obtained under various conditions, generalising reaction types & schemes, predict catalyst performance…
  - Catalyst development
    - Material synthesis, structure properties, catalyst stability, compatibility…
  - Analysis techniques
    - Detection limits in terms of dimension of time & size and under extreme conditions (T, P) and accuracy of measurements, microscopic techniques, sample preparation techniques…
  - Reaction modelling
    - Elementary reactions and rates, quantum mechanics/chemistry, physical chemistry …
  - Reactor modelling
    - Mathematical interpretation and representation, the numerical method, micro-kinetics, structure and efficiency of heat and mass transfer in relation to reactor design …
  - Catalytic process
    - Heat and mass transfers, energy balance and efficiency of process …

Catalytic Reaction Processes

- **Understanding catalytic reaction processes**
  - **A catalytic reaction can be operated in a *batch* manner**
    - **Reactants and catalysts are loaded together in reactor and catalytic reactions (homo- or heterogeneous) take place in pre-determined temperature and pressure for a desired time / desired conversion**
    - **Type of reactor is usually simple, basic requirements**
      - **Withstand required temperature & pressure**
      - **Some stirring to encourage mass and heat transfers**
      - **Provide sufficient heating or cooling**
  - **Catalytic reactions are commonly operated in a *continuous* manner**
    - **Reactants, which are usually in gas or liquid phase, are fed to reactor in *steady* rate (e.g. mol/h, kg/h, m^3/h)**
    - **Usually a *target conversion* is set for the reaction, based on this target**
      - **required quantities of catalyst is added**
      - **required heating or cooling is provided**
      - **required reactor dimension and characteristics are designed accordingly.**

Catalytic Reaction Processes

- **Catalytic reactions in a *continuous* operation (*cont'd*)**
  - **Reactants in continuous operation are mostly in gas phase or liquid phase**
    - **easy transportation**
    - **The heat & mass transfer rates in gas phase is much faster than those in liquid**
  - **Catalysts are pre-loaded, when using a solid catalyst, or fed together with reactants when catalyst & reactants are in the same phase and pre-mixed**
    - **It is common to use solid catalyst because of its easiness to separate catalyst from unreacted reactants and products**

      Note: In a chemical process separation usually accounts for ~80% of cost. That is why engineers always try to put a liquid catalyst on to a solid carrier.
    - **With pre-loaded solid catalyst, there is no need to transport catalyst which is then more economic and less attrition of solid catalyst** (Catalysts do not change before and after a reaction and can be used for number cycles, months or years)**,**
    - **In some cases catalysts has to be transported because of need of *regeneration***
- **In most cases, catalytic reactions are carried out with catalyst in a fixed-bed reactor (fluidised-bed in case of regeneration being needed), with the reactant being gases or liquids**

Catalytic Reaction Processes

- **General requirements for a good catalyst**
  - **Activity - being able to promote the rate of desired reactions**
  - **Selective - being to promote only the rate of desired reaction and also retard the undesired reactions**

    Note: The selectivity is sometime considered to be more important than the activity and sometime it is more difficult to achieve

    (e.g. selective oxidation of NO to NO_2 in the presence of SO_2)
  - **Stability - a good catalyst should resist to deactivation, caused by**
    - **the presence of impurities in feed (e.g. lead in petrol poison TWC.**
    - **thermal deterioration, volatility and hydrolysis of active components**
    - **attrition due to mechanical movement or pressure shock**
  - **A solid catalyst should have reasonably large surface area needed for reaction (active sites). This is usually achieved by making the solid into a porous structure.**

Catalysis ; pengantar

Mekanisme umum:

Reaktan + katalis → "kompleks"

Compleks → Produk + Katalis

Klasifikasi Katalis

- Katalis Homogen
- Katalis Heterogen
- Katalis Biologis (Enzyme)

Katalis Homogen

- Katalis homogen adalah zat yang berfasa sama dengan fasa yang bereaksi yang ditambahkan untuk mempercepat suatu reaksi
- Contoh:

  Katalis asam/basa, inisiator radikal, pelarut dsb.

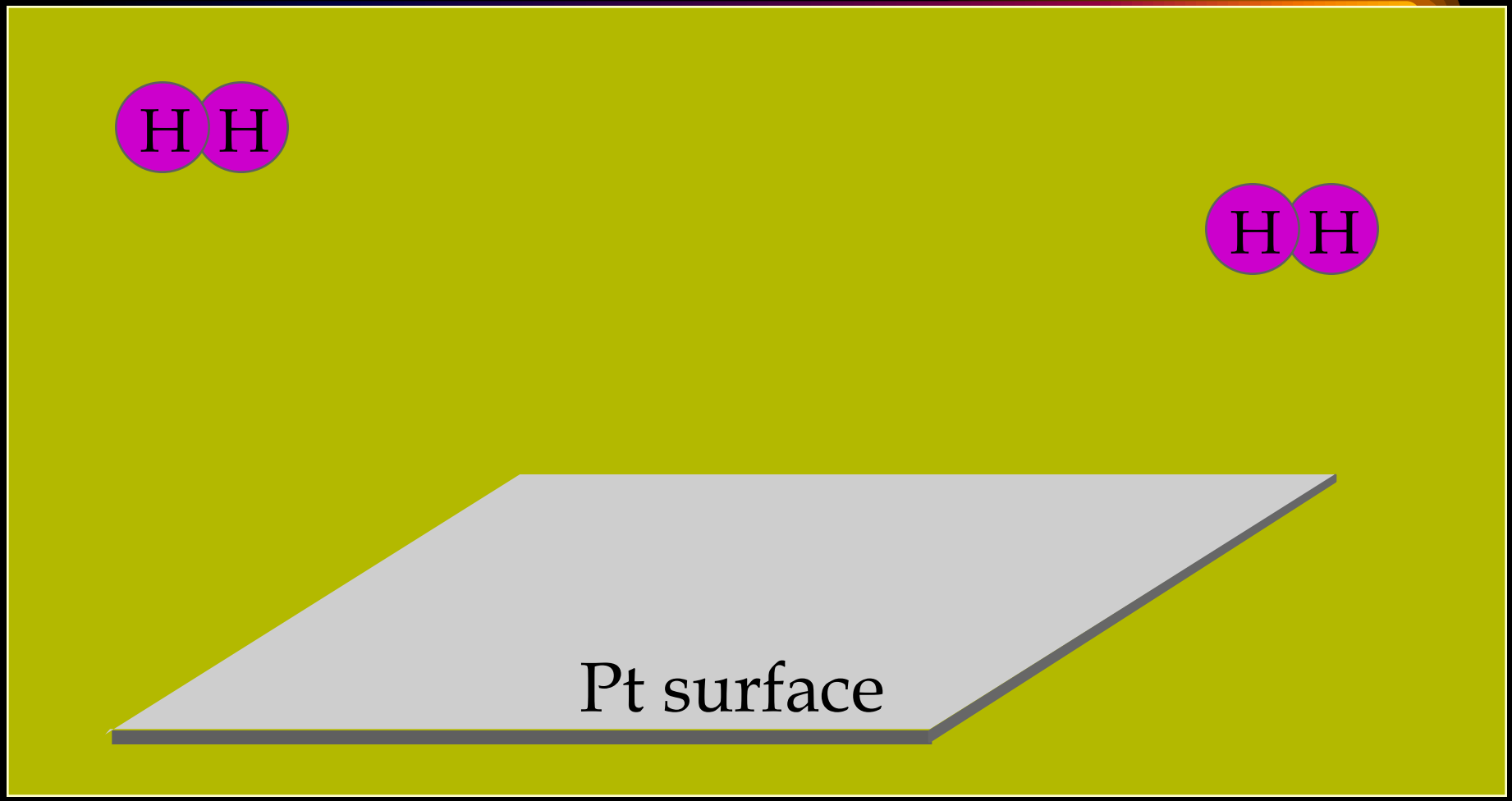
$$C_2H_2 + C_6H_6 \xrightarrow{H^+} CH_3CH_2C_6H_5$$

$$H^+ + C_2H_2 \longrightarrow [CH_3CH_2]^+$$

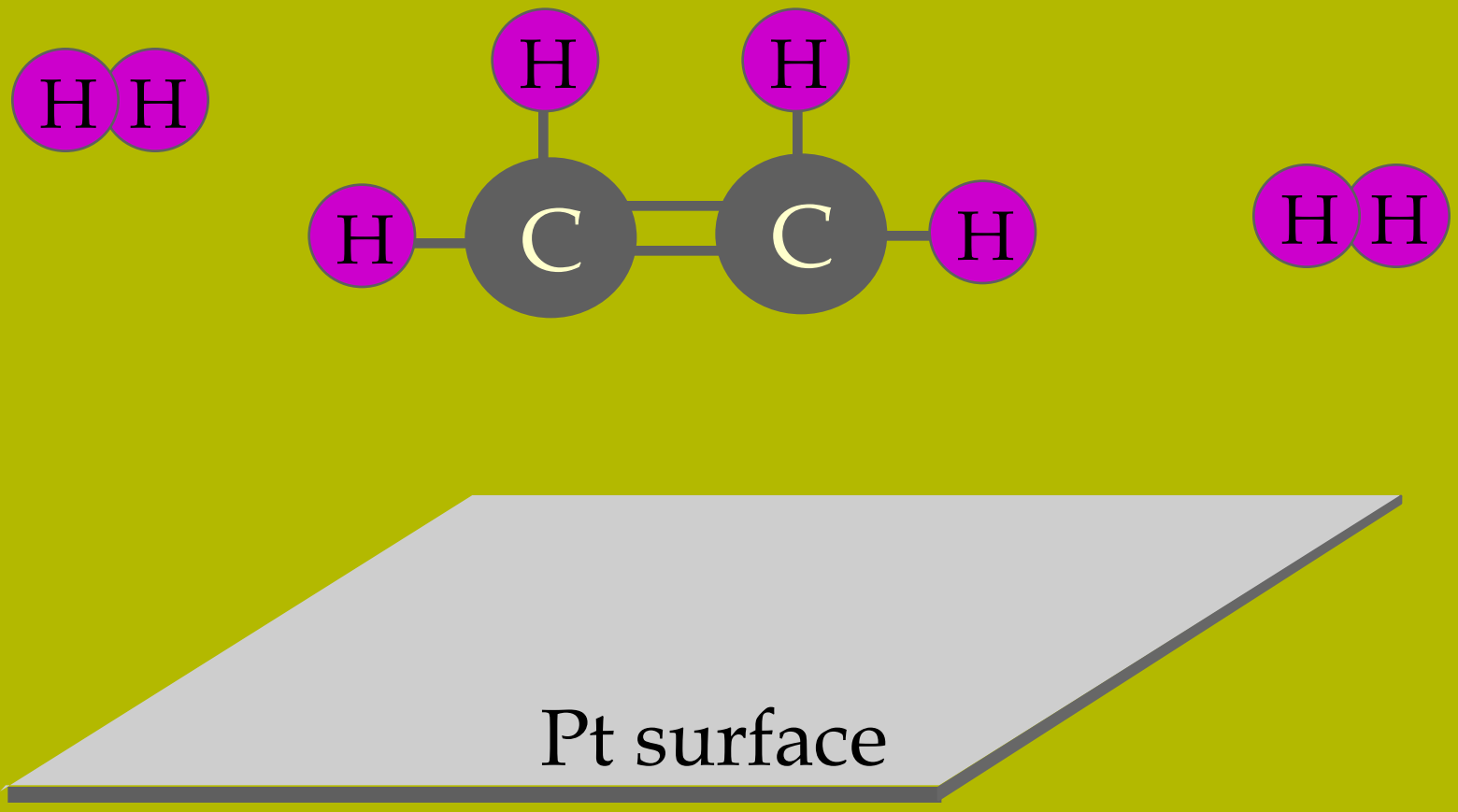
$$[CH_3CH_2]^+ + C_6H_6 \longrightarrow [CH_3CH_2C_6H_6]^+$$

$$[CH_3CH_2C_6H_6]^+ \longrightarrow CH_3CH_2C_6H_5 + H^+$$

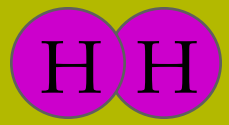
Katalis Heterogenous



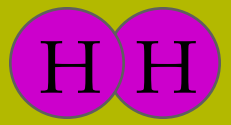
Katalis Heterogenous

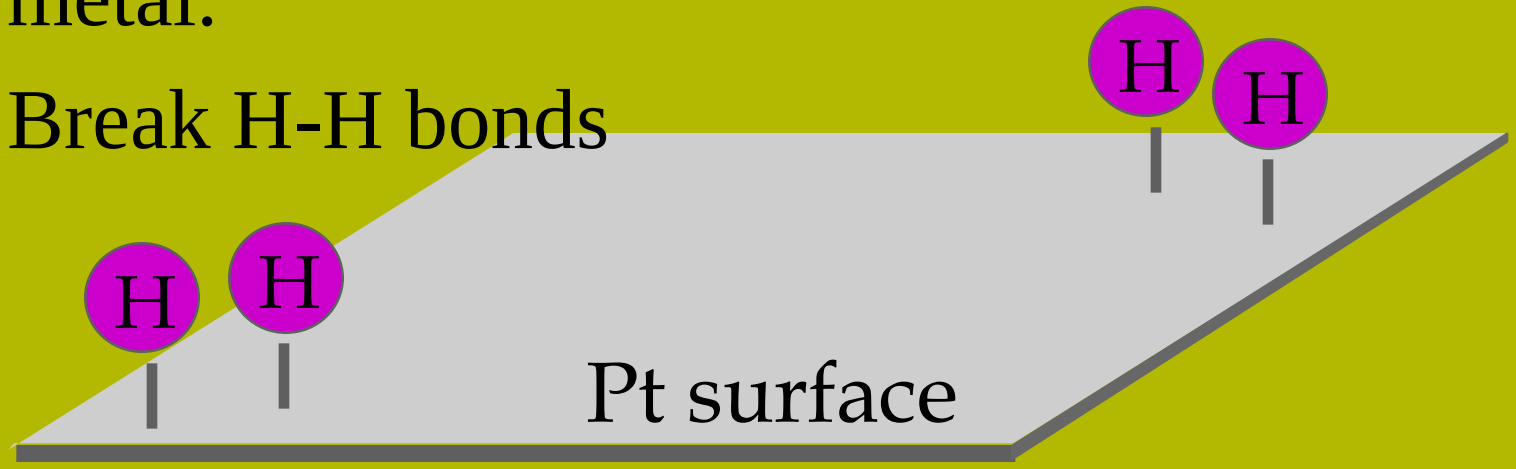


Heterogenous Catalysts

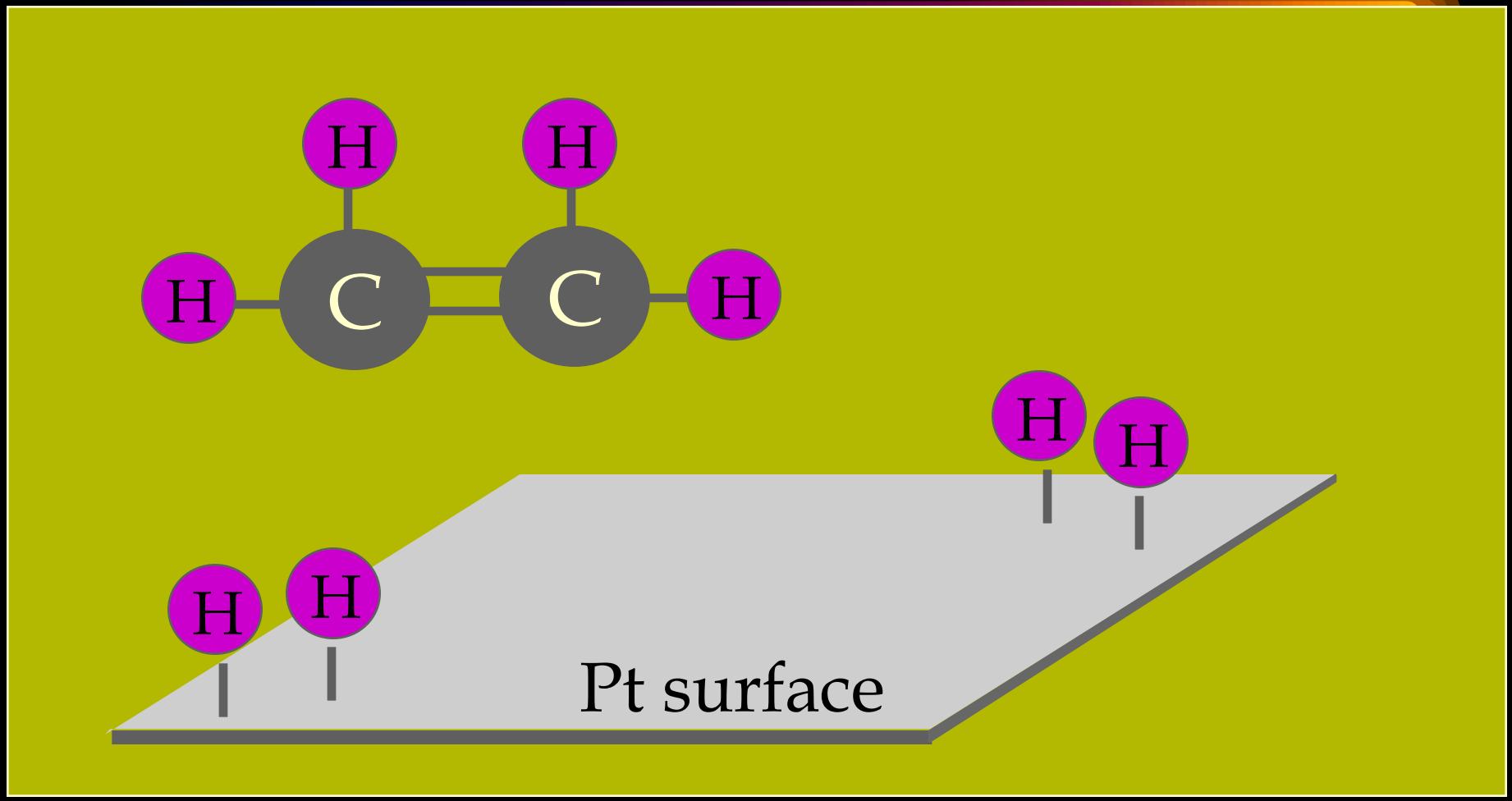


- Hydrogen bonds to surface of metal.
- Break H-H bonds



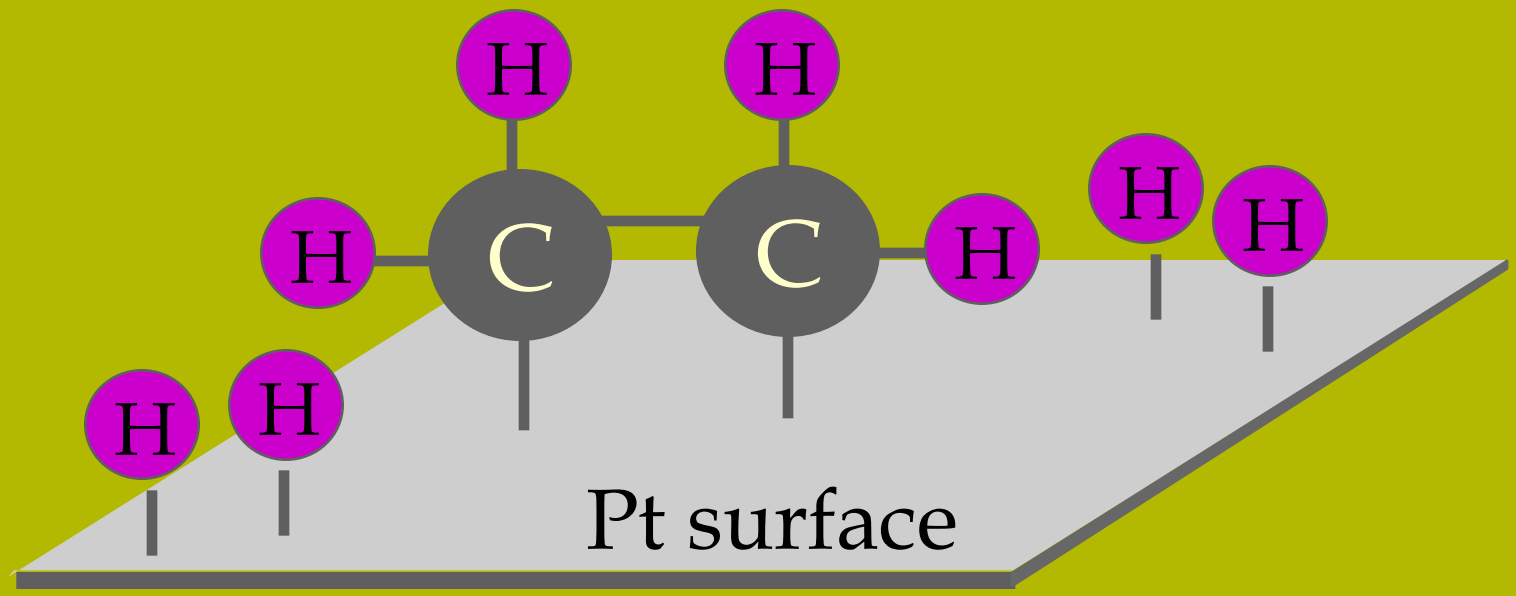


Heterogenous Catalysts



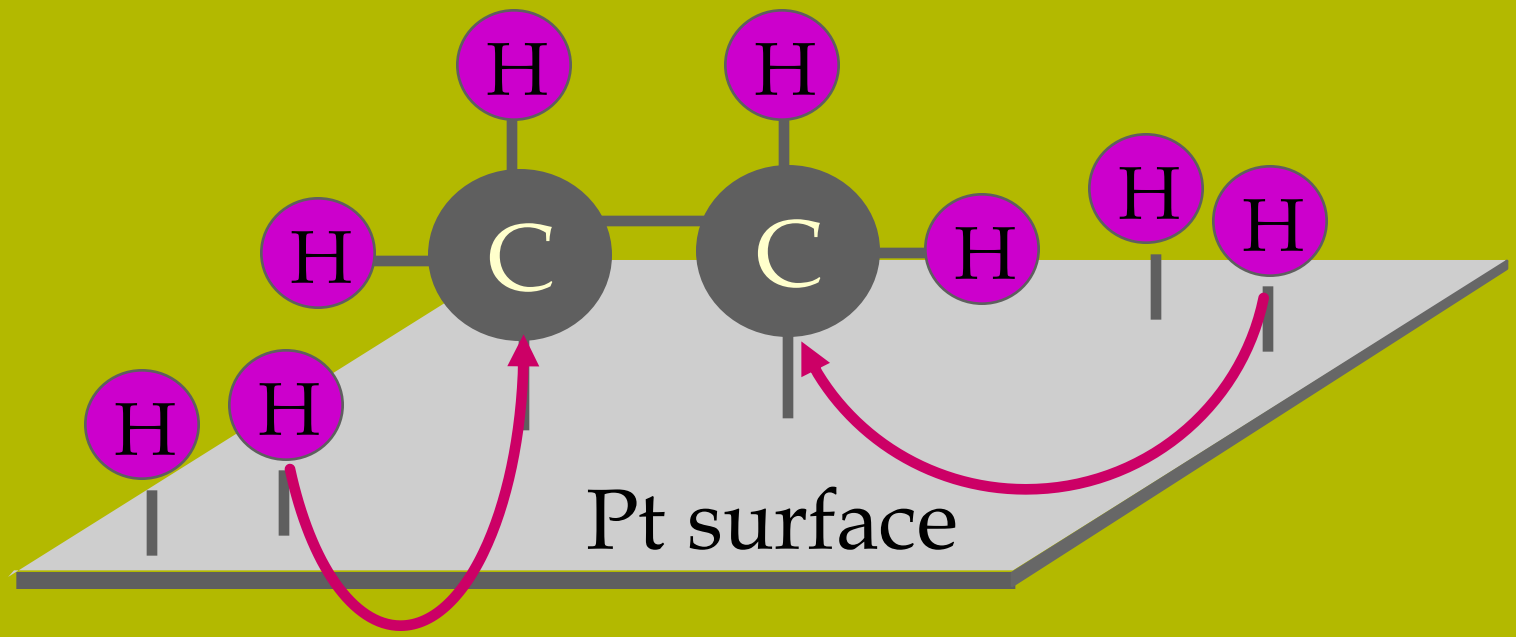
Heterogenous Catalysts

- The double bond breaks and bonds to the catalyst.



Heterogenous Catalysts

- The hydrogen atoms bond with the carbon



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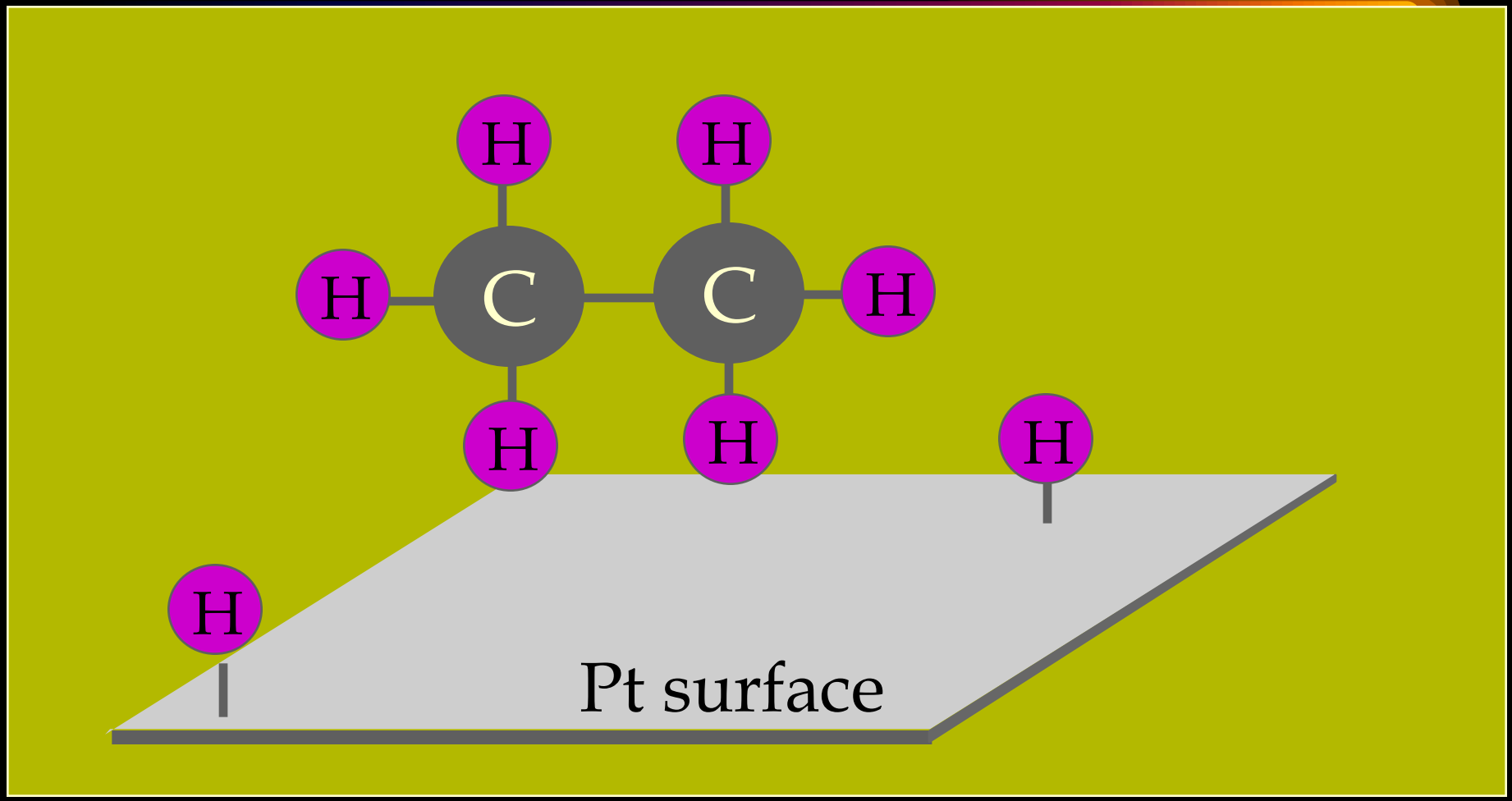

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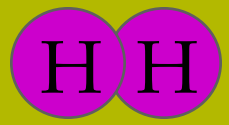

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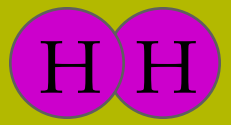

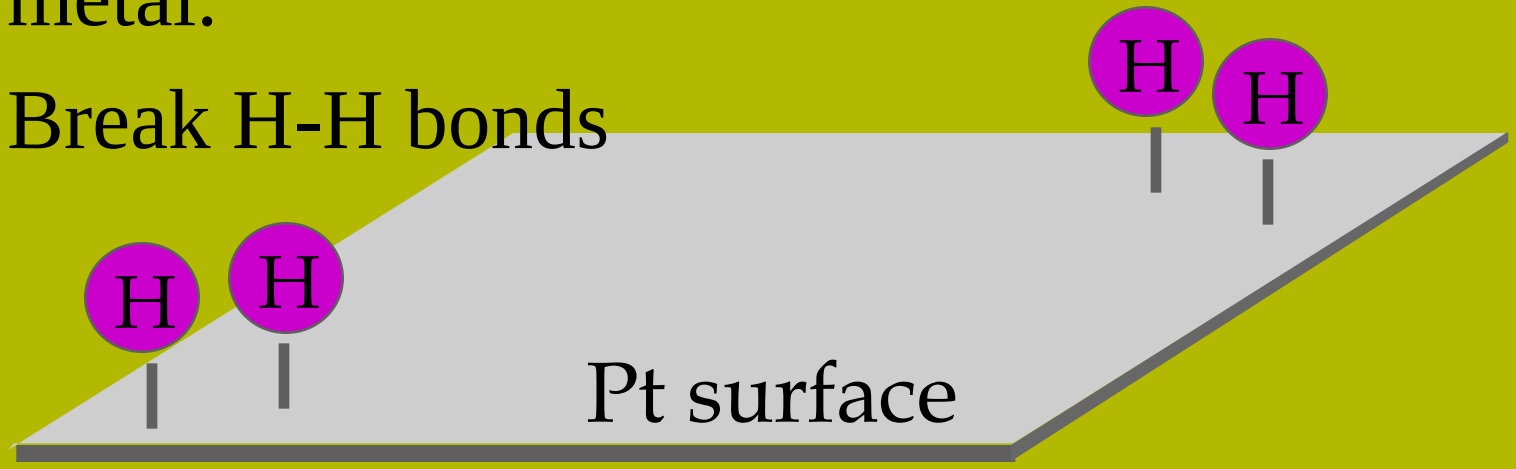

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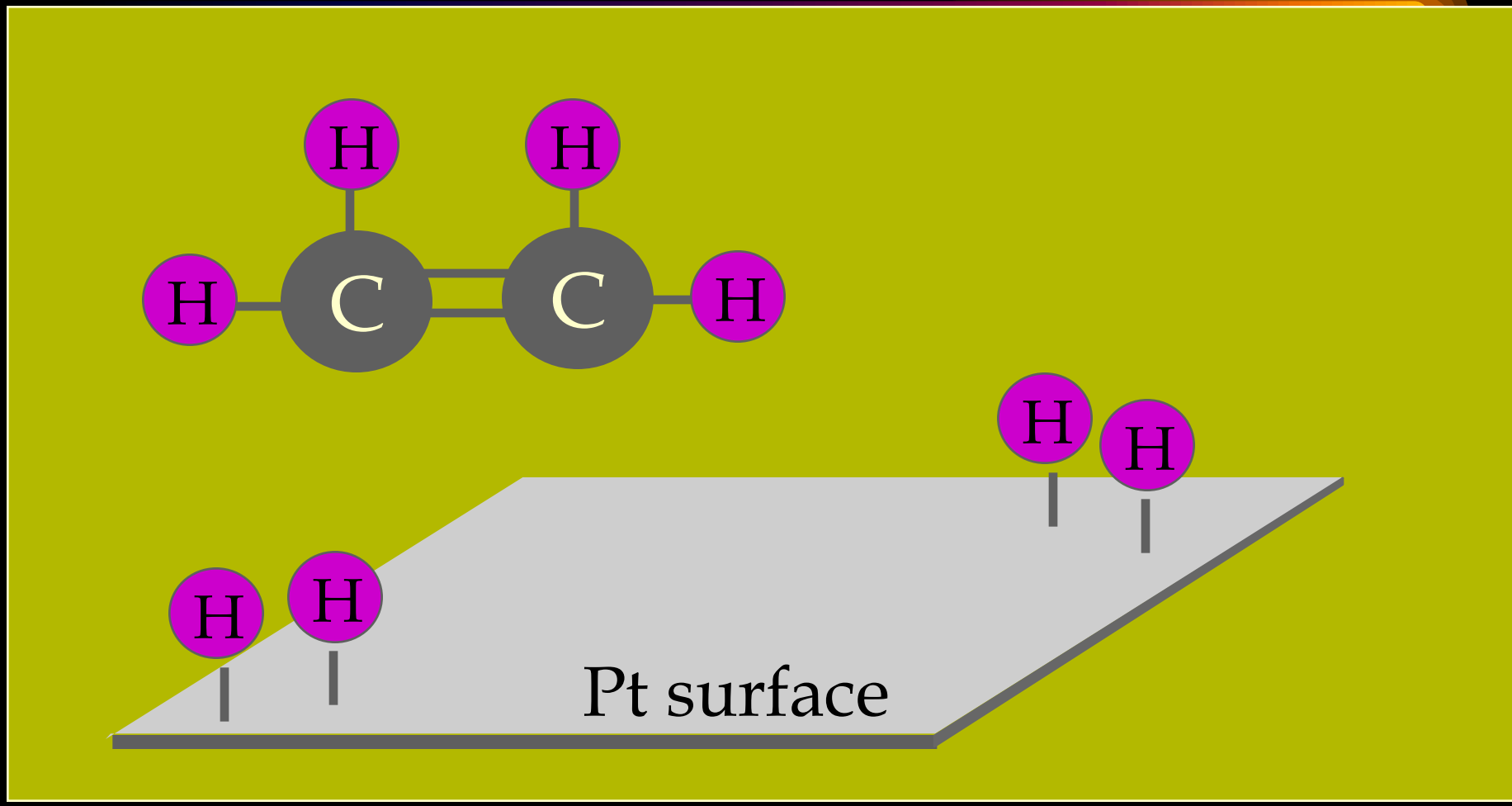

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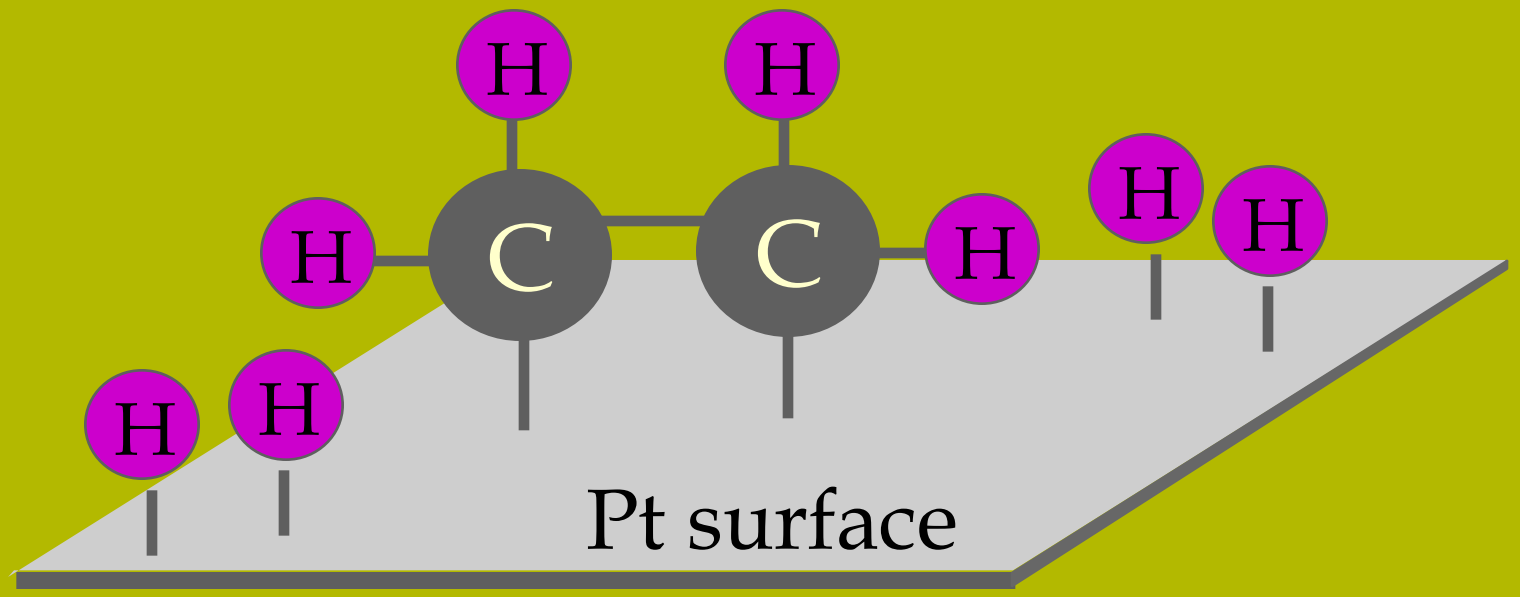

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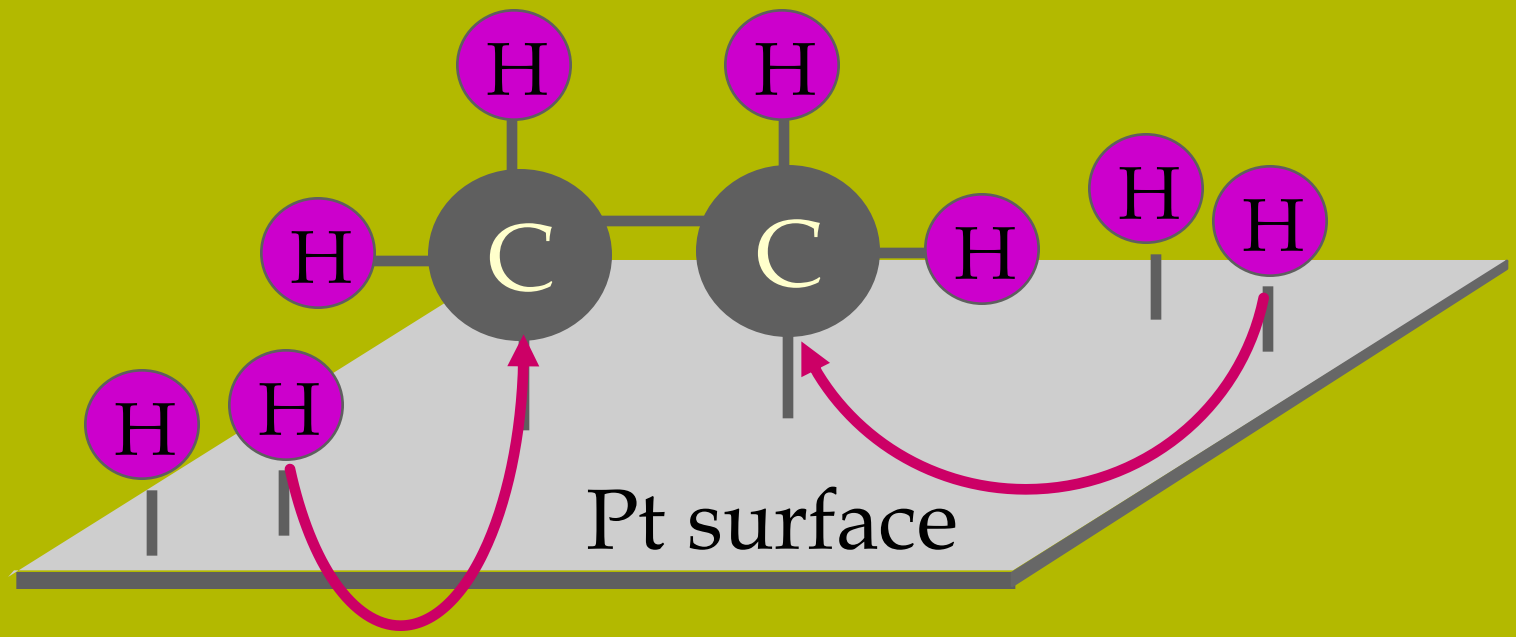
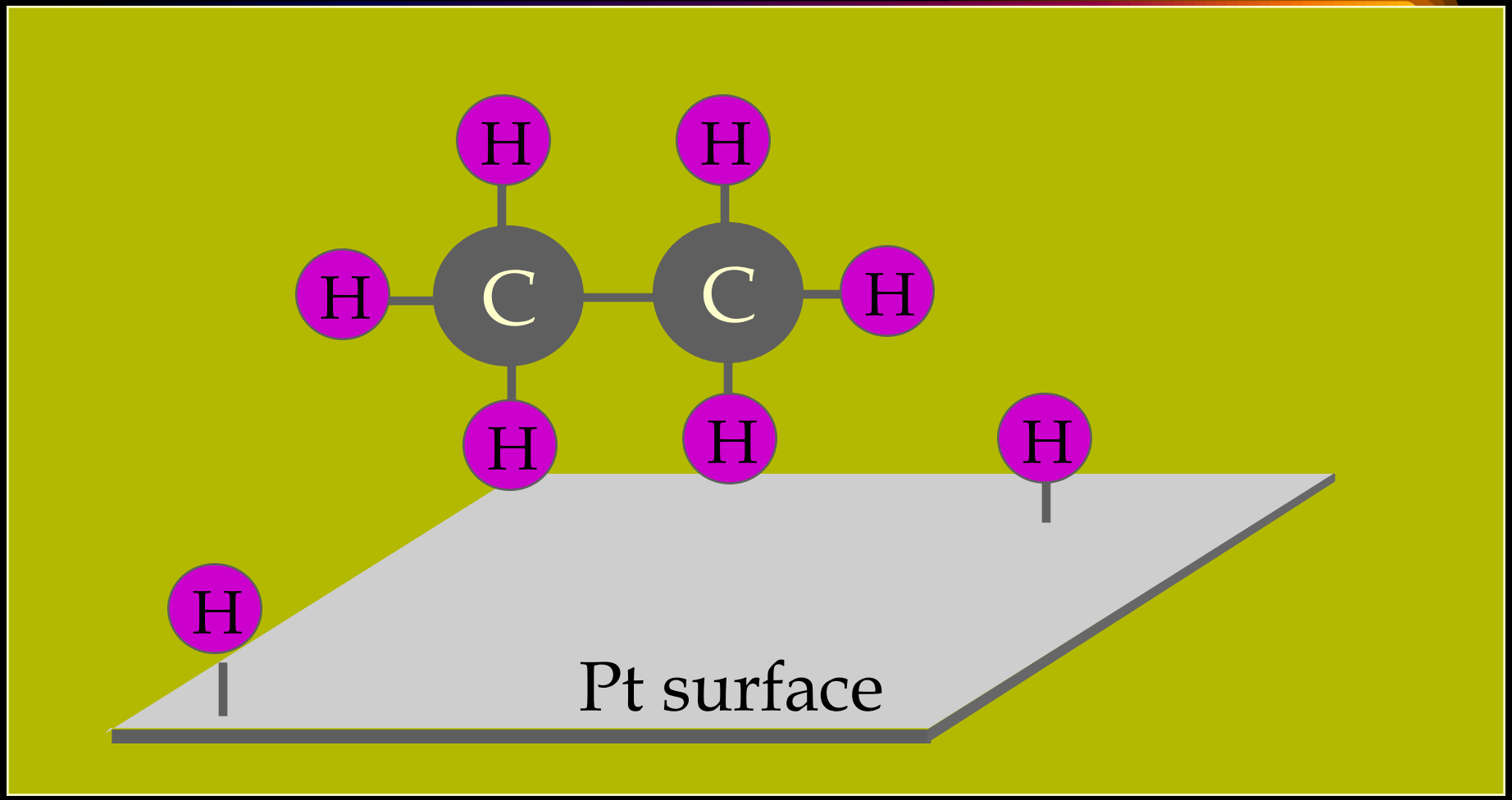


Heterogenous Catalysts



Kinetika Reaksi Katalitik

Kasus Khusus: Reaksi gas pada permukaan logam

- Reaksi gas pada permukaan logam memiliki peranan penting dalam berbagai proses:

Hidrogenasi

$$N_2 + 3H_2 \xrightarrow{Fe/K} 3NH_3$$

Produksi pupuk dan as. nitrat

$$C_2H_4 + 3H_2 \xrightarrow{Ni} C_2H_6$$

Peningkatan Mutu minyak bumi/angka oktane

Dehidrogenasi

$$C_2H_4 \xrightarrow{Pt} C_2H_2 + H_2$$

Produksi Monomer

Oksidasi

$$2CO + 2NO \xrightarrow{Pt/Rh} 2CO_2 + N_2$$

Katalitik Konverter

$$C_2H_4 + \tfrac{1}{2}O_2 \xrightarrow{Pt} C_2H_4O$$

Produksi monomer

Keterangan:

Kinetika Reaksi Katalitik

Kasus Khusus: Reaksi gas pada permukaan logam

Reaksi fasa gas dg inisiator radikal (X)

$$X + H_2 \rightarrow 2H + X$$

$$X + O_2 \rightarrow 2O + X$$

Inisiasi

$$O + H_2 \rightarrow OH + H$$

$$H + O_2 \rightarrow OH + O$$

Propagasi

$$X + 2H \rightarrow H_2 + X$$

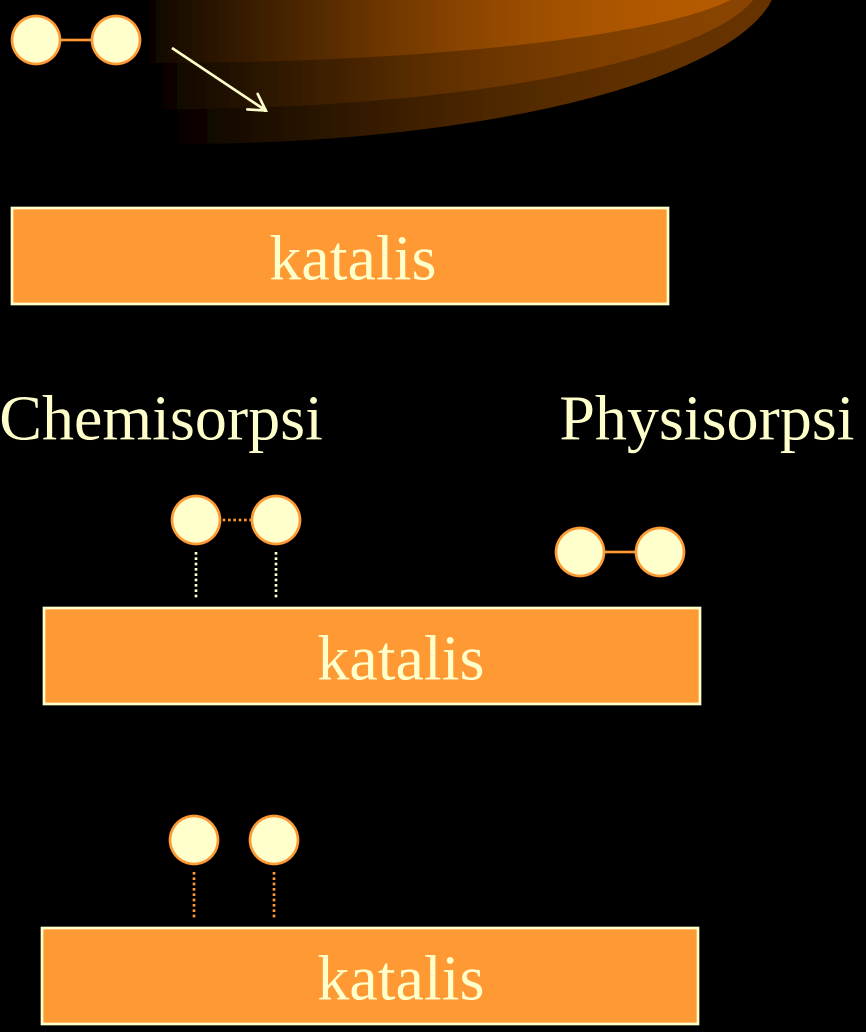
Terminasi

Kinetika Reaksi Katalitik

Kasus Khusus: Reaksi gas pada permukaan logam

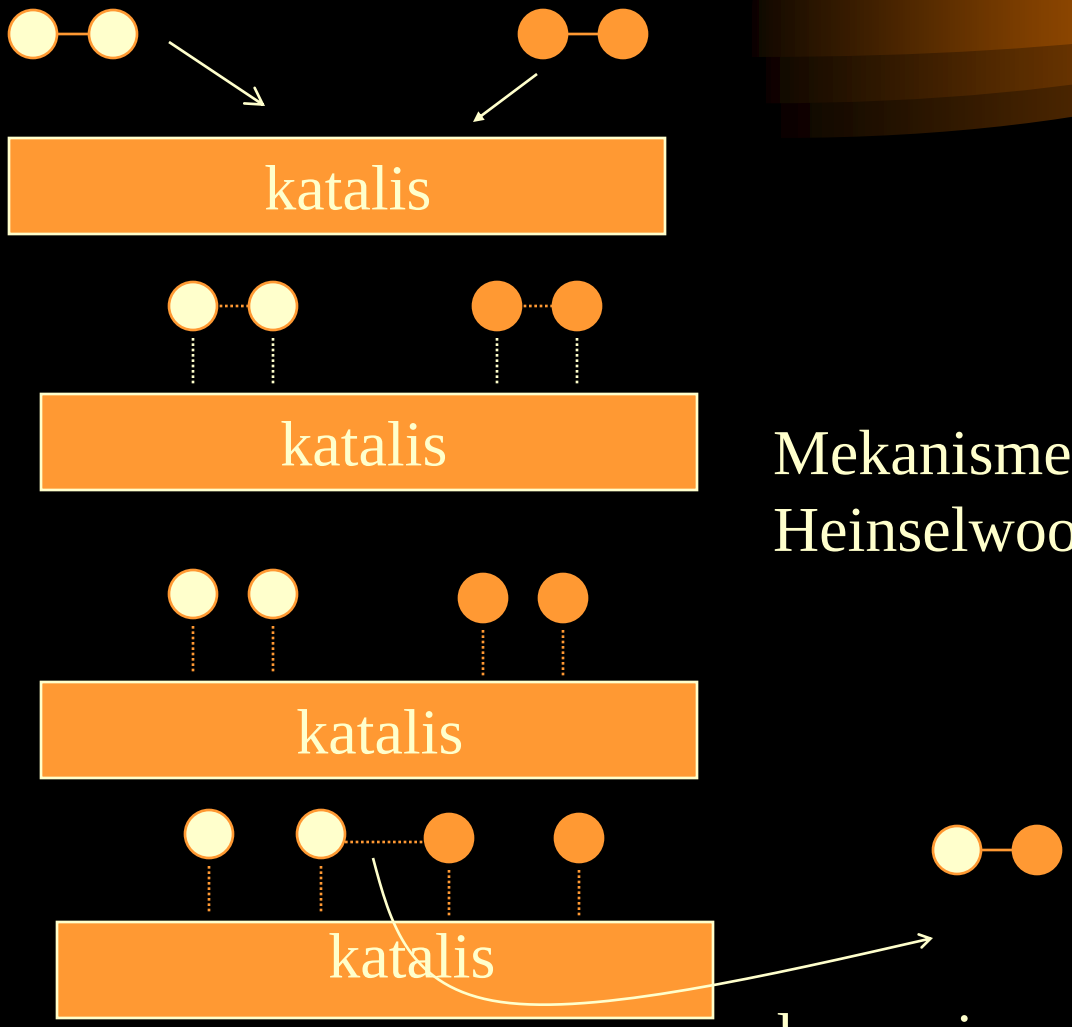
Mekanisme umum:

- Adsorpsi
- Disosiasi
- Reaksi
- Desorpsi produk



Kinetika Reaksi Katalitik

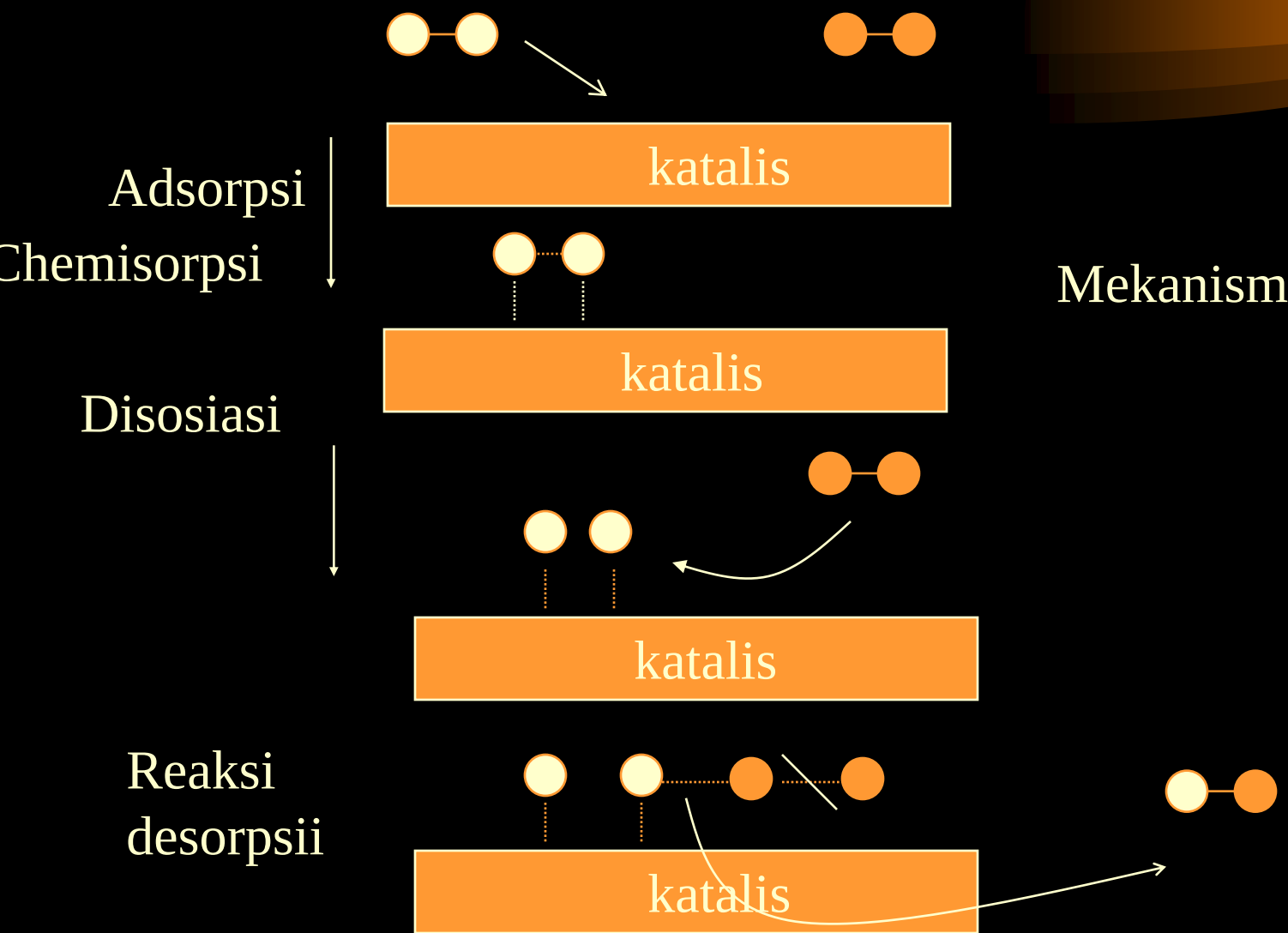
Kasus Khusus: Reaksi gas pada permukaan logam



Mekanisme Langmuir-Heinselwood

Kinetika Reaksi Katalitik

Kasus Khusus: Reaksi gas pada permukaan logam



Mekanisme Eley Rideal

Kinetika Reaksi Katalitik

Kasus Khusus: Reaksi gas pada permukaan logam

Langmuir Hinshelwood

$$N_2 + 6S \rightarrow 2N_{(ad)}$$

$$H_2 + 2S \rightarrow 2H_{(ad)}$$

$$N_{(ad)} + H_{(ad)} \rightarrow NH_{(ad)} + 2S$$

$$NH_{(ad)} + H_{(ad)} \rightarrow NH_{2(ad)} + 2S$$

$$NH_{2(ad)} + H_{(ad)} \rightarrow NH_{3(ad)} + 2S$$

Eley Rideal

$$N_2 + 6S \rightarrow 2N_{(ad)}$$

$$N_{(ad)} + H_2 \rightarrow NH_{(ad)} + H_{(ad)}$$

$$NH_{(ad)} + H_2 \rightarrow NH_{2(ad)} + H_{(ad)}$$

$$NH_{2(ad)} + H_2 \rightarrow NH_{3(ad)} + H_{(ad}$$

$$2H_{(ad)} \rightarrow H_2 + 2S$$

Kinetika Reaksi Katalitik

Kasus Khusus: Reaksi gas pada permukaan logam

$$r_C = k_3[A_{ad}] - k_4[C_{ad}]$$

- Laju reaksi menjadi:

$$r = \frac{k_3 K_A P_A S_0 - k_4 K_C P_C S_0}{1 + K_A P_A + K_B P_B + K_C P_C}$$

- Jika $k_4 = 0$:

$$r = \frac{k_3 K_A P_A S_0}{1 + K_A P_A + K_B P_B + K_C P_C}$$

- Jika didefinisikan

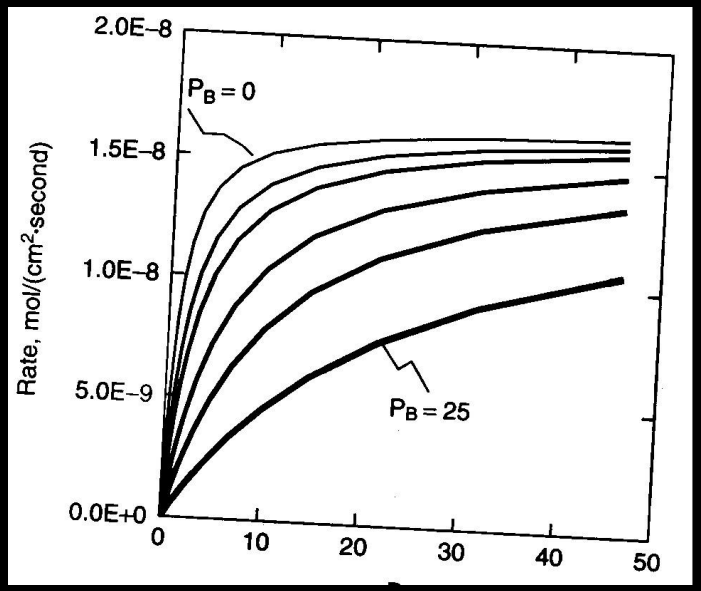
$$\theta_A = \frac{[A_{ads}]}{S_0}$$

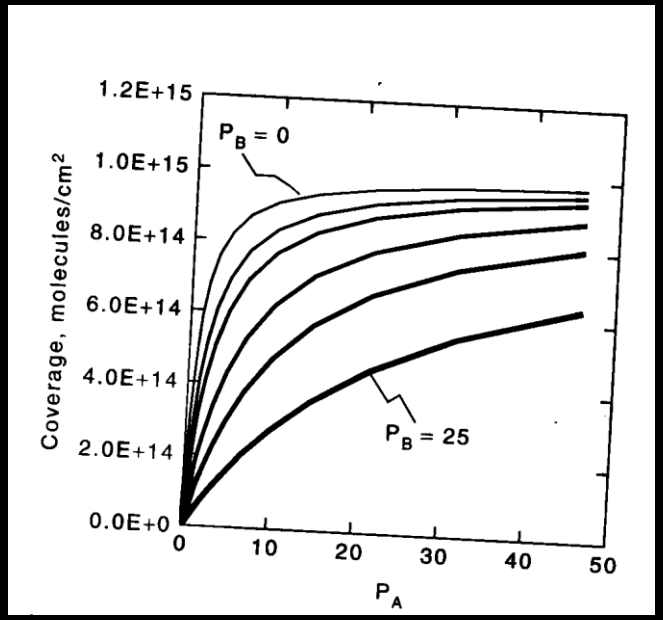
$$\theta_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B + K_C P_C}$$

Kinetika Reaksi Katalitik

Kasus Khusus: Reaksi gas pada permukaan logam

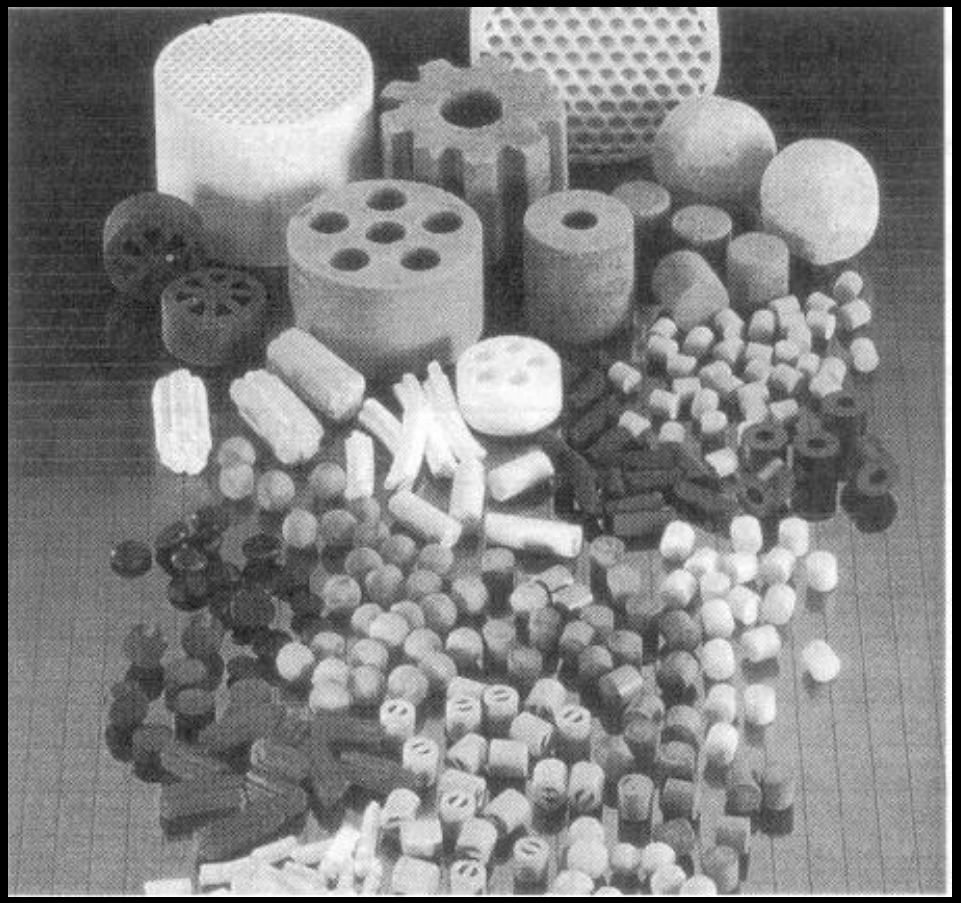
- Isotherm Langmuir,





Katalisis pada proses Industri

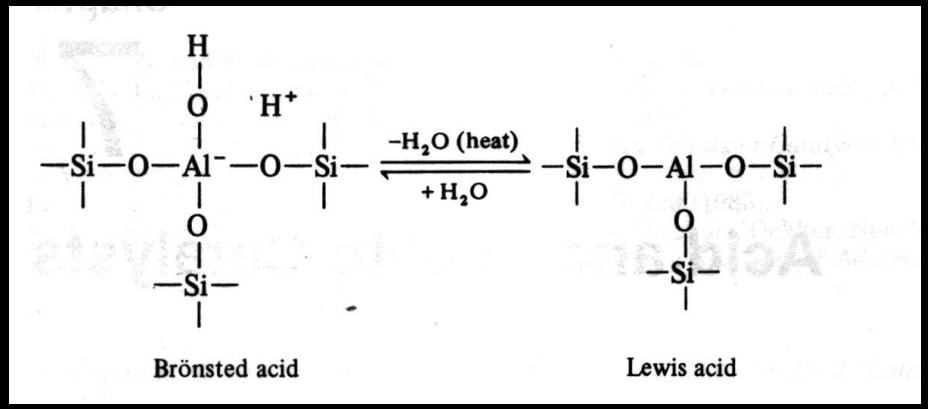
Kasus Khusus: Katalis Asam (Zeolite)



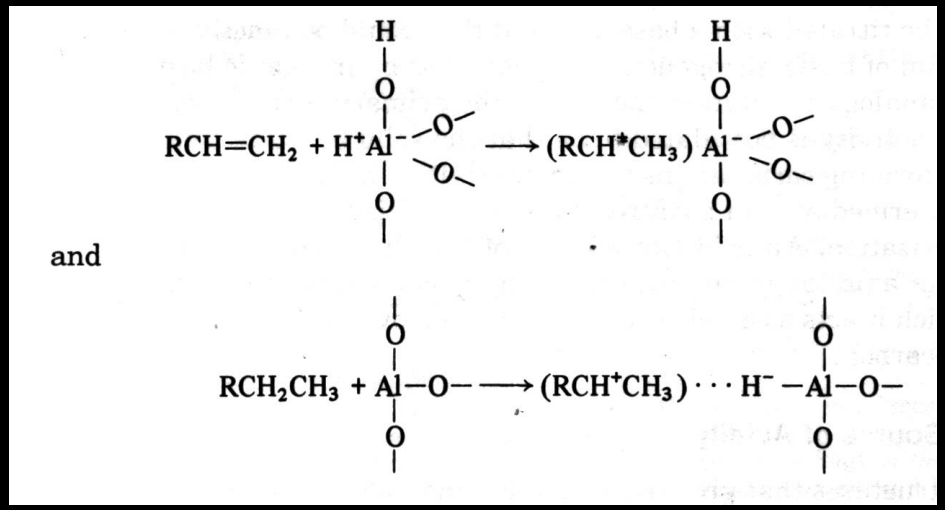
- Konsep bahwa padatan dapat bersifat asam muncul dari pengamatan bahwa reaksi-reaksi hidrocarbon dapat “dikatalisis” dengan andanya lempung asam atau silica-alumina

Katalisis pada proses Industri

Kasus Khusus: Katalis Asam (Zeolite)



Sifat Asam Katalis Padat



Zeolite merupakan padatan silika-alumina yang dapat berperan sebagai katalis asam

Katalisis pada proses Industri

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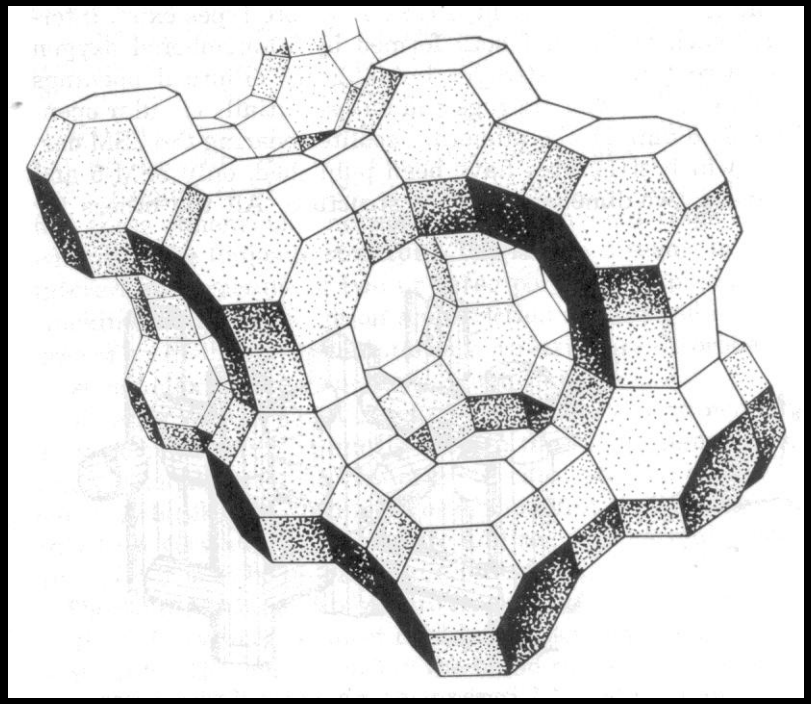
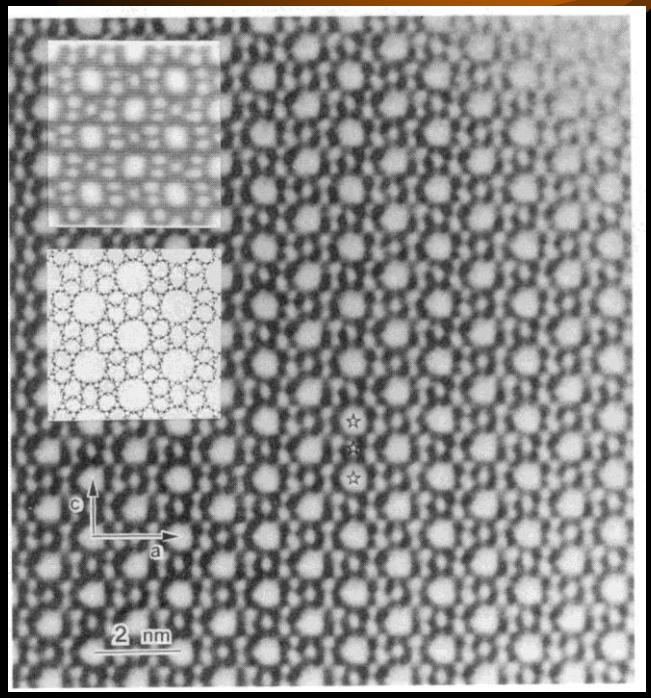


Visualisasi Struktur Zeolith/Fauzaite



SEM image dari ZSM-5

Katalisis pada proses Industri

Kasus Khusus: Katalis Asam (Zeolite)

- Keistimewaan Material Zeolite:

  - Memiliki struktur pori pada ukuran molekuler (0.3 – 1 nm)

  - Sebagai katalitik reaktor yang selektif