King Saud University
College of Science
Chemistry Department

جامعة الملك سعود
King Saud University

Organic Industries

CHEM 442

For BSc Students; Chemistry Program

Credit hrs.: 2 (1+1)

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Introduction

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- What is industrial chemistry?
- Raw materials for the chemical process industries
  - Petroleum and its products,
  - natural gas and
  - biomass conversion.
- Industrial catalysis;
  - Choice of catalysis,
  - homogenous and heterogeneous catalysis.

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What Is Industrial Chemistry?

- Industrial Chemistry *is the manufacturing art concerned with the transformation of raw materials into useful materials in useful amounts*.
- This transformation involves some kind of process following a recipe.
  - grinding,
  - mixing together various ingredients,
  - dissolving,
  - heating,
  - cooling,
  - evaporating or distilling,
  - growing crystals,
  - filtering,
  - and other physical-chemical-biological operations.

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What Is Industrial Chemistry?

- Some of the oldest examples include:
  - Leavened bread.
  - brewing beer.
  - Soap.
  - Charcoal.
  - The seven metals known to the ancients (gold, silver, copper, tin, lead, iron, and mercury),

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What Is Industrial Chemistry?

The history of industrial chemistry is linked to building blocks

- 1850- Plants, Animals
- 1850+ Coal Tar (side product of "coal gasification")
- 1920+ Acetylene (from CaC_2, Reppe Chemistry)
- 1950+ Ethylene (from oil)
- 1973+ CH_4, CO/H_2 (syngas)

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What Is Industrial Chemistry?

What is a building block?

- A *building block* is any (organic) chemical that can be used to synthesize other (organic) chemicals.
- There are very few truly primary, large-volume organic building blocks.
- These are all currently obtained from:
  - Petroleum refining
  - Natural gas
  - Coal
  - Ammonia
  - Carbon dioxide
  - Renewable resources

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Building blocks: Primary, secondary, ...

1° BB	2° BB	3° BB
▪ Ethylene	Ethylene dichloride Ethylene oxide Ethyl benzene	Vinyl chloride Ethylene glycol Vinyl acetate
▪ Propylene	▪ Propylene oxide ▪ Acrylonitrile ▪ Isopropyl alcohol ▪ Cumene ▪ *n*-Butyl alcohol	▪ Acetone
▪ Benzene	▪ Ethyl benzene ▪ Cumene	▪ Styrene ▪ Phenol ▪ Acetone ▪ Bisphenol A
▪ Methanol	▪ Acetic acid ▪ formaldehyde	▪ Vinyl acetate
▪ Toluene ▪ Xylenes	▪ Terphthalic acid	▪ Polyester

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What Is Industrial Chemistry?

- Chemistry *is now defined as the science of the nature of matter and its transformations.*
- The science of chemistry can be exploited as
  - An analytical or diagnostic tool,

    are about information and knowledge, and the amount of physical material required may be as small as can be conveniently manipulated, often fractions of a gram.
  - or to make materials to be used for some purpose.

    is about making materials in quantity.

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What Is Industrial Chemistry?

- These materials range from
  - Natural (biological) products like cotton, wool, rubber, and paper.
  - Inorganics like steel, copper, aluminum, brick, concrete, glass, fertilizer, acids, and alkalis.
  - Fuels like methane gas, gasoline, diesel, and kerosene.
  - Polymers like polyethylene, polystyrene, polyester, and nylon; and
  - Fine chemicals like paints and adhesives, pigments and dyes, soap and detergents, solvents, fire retardants, explosives, pesticides, vitamins, pharmaceuticals.
- The process used to manufacture the product may be operated in batch or continuous sequences.

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What Is Industrial Chemistry?

- *Laboratory-scale chemical methods* are used for experimentation and for very-small-scale manufacture.
  - The annual production of some of these materials is less than a few kgs per year.
  - Equipment used like beakers and flasks have volumes from a few milliliters to a few liters.
  - Temperatures generally range from 50°C to 250°C at pressures around 1 bar,

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What Is Industrial Chemistry?

- *Specialty scale industrial chemical methods* are most often also conducted in batch mode, following a recipe.
  - Annual production greater than that up to about 1000 tones per year is considered.
  - The equipment (*designed, constructed, and connected together only for the production of one specific chemical*) is larger with volumes up to a few thousand liters,
  - The sequence of steps may be almost identical to those used at the smaller lab scale.
  - At larger than lab scale, many more considerations become important including *consistency*, *reliability*, *environmental impact*, *economics*, *specialized expertise in process*, *equipment design* & *operation*, and *chemical knowledge*.
- *Commodity scale;* Annual production greater than 1000 tones per year is.

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What Is Industrial Chemistry?

Cost considerations

- Capital costs: The one-off cost of constructing the plant and all the associated costs of all buildings.
- Variable costs: The cost that changes throughout the year and is dependant on how much product is sold. e.g. Buying raw materials, treating waste and despatching the product.
- Fixed costs: The annual cost of the staff, local rates, advertising and utility bills.

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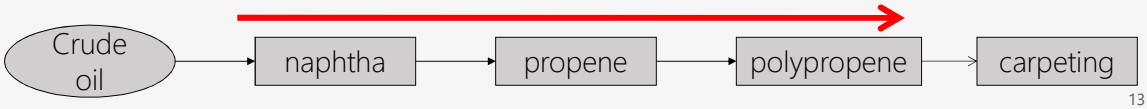
What Is Industrial Chemistry?

Choices to be made

1. Cost, availability of feedstock's
2. Yield of the reaction
3. Can un-reacted materials be recycled?
4. Can by-products be sold?
5. Cost of waste disposal
6. Energy consumption, generating your own, conservation, use of catalysts, recycling of heat, (heat exchangers),
7. Environmental issues

Value added, e.g. increasing the value of the products from crude oil



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What Is Industrial Chemistry?

- Saudi Arabia is among the twenty most important industrial and emerging countries (*G-20*).
- Saudi Arabia is the main member of the OPEC (*Organization of the Petroleum Exporting Countries*) countries.
- Saudi Arabia possesses the largest conventional oil reserves worldwide ,
- Saudi Arabia's industry sectors are dominated by *petrochemicals* and *petrochemical based products*.
- The main industries in Saudi Arabia include *crude oil production*, *petroleum refining*, *ammonia*, *industrial gases*, *sodium hydroxide*, *fertilizers*, *cement*, *plastics*, *metals*.

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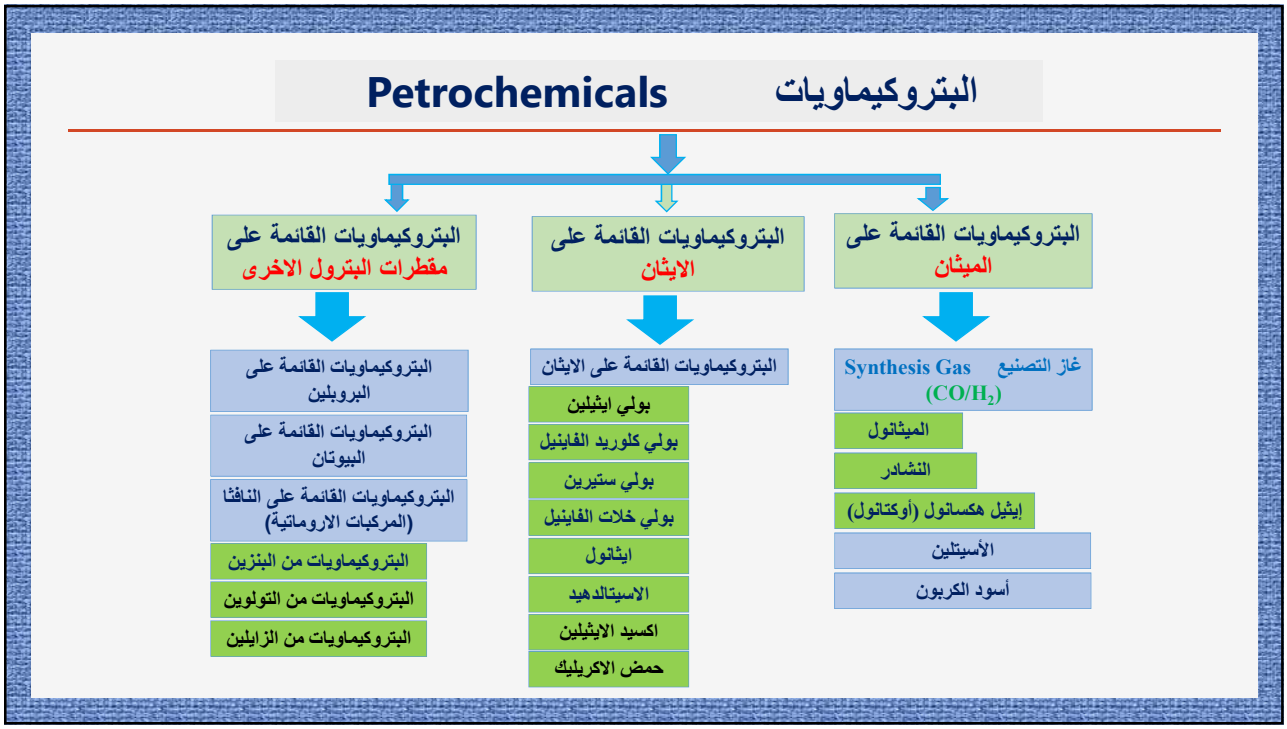

Saudi chemicals output

- The Chemicals industry is an essential part of the Kingdom's economic diversification.
- In line with Vision 2030, we have the ambition to further double its value.

170 Billion SAR Operating revenues of the Chemicals sector for 2016

5% Production capacity growth for Chemicals for 2016

97,267 KT Chemical production capacity in KSA for 2017

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Saudi Arabia Industry Sectors: Oil and Gas

- Saudi Arabia will account for 20.83% of the Middle Eastern regional oil demand by 2013, while providing 39.45% of the supply.
- Oil use is expected to increase to 12.17 million b/d by 2013, while oil production is expected to rise to 28.01 million b/d by 2013.
- State owned Saudi Aramco's oil and gas production is expected to rise to 11.05 million b/d by 2013.
- Saudi Arabia's oil production is forecasted to grow 14.3% by 2018, with volumes steadily rising to 12.4 million b/d by 2018. Oil consumption is expected to increase by 30.9% by 2018.

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BASIC CHEMICAL INDUSTRIES (BCI)

THE INDUSTRY LEADER

- Since its inception in 1973, Basic Chemical Industries (BCI) has grown impressively to become one of the leading chemical companies in the Kingdom of Saudi Arabia.
- Located in the Eastern Province of the Kingdom, the company's headquarters, its manufacturing plant and main storage facilities are on its own 200,000 square meter site besides Dammam' s First Industrial City.
- BCI is 100% Saudi owned and for over 40 years has been supporting the Saudi industrial and consumer market by providing high quality chemical products.
- From the outset the company's expansion and innovation programs have been a continuous process of adopting the latest methods of research and production which has maintained BCI as the leader in its field.

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Raw Materials For The Chemical Process Industries

- Chemical process industries uses raw material derived from
  - **Petroleum and its products**
  - **Natural gas**
  - **Biomass conversion**
- More than 90% of organic chemicals are produced from petroleum and natural gas routes.
- **Raw materials for chemical industries are classified as**
  - Primary raw materials and
  - Basic intermediates.

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Raw Materials For The Chemical Process Industries

- Primary raw materials *are naturally occurring substances that have not been subjected to chemical changes after being recovered.*
- Examples of raw materials:
  - Grains such as wheat and rice
  - Vegetables such as carrots and onions
  - Meat such as beef and chicken
  - Wood from a tree
  - Honey from a bee's nest
  - Crude oil.

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Raw Materials For The Chemical Process Industries

Secondary Intermediates:

Monomers: caprolactam, adipic acid, hexamethylene diamine, terephthalic acid and acrylonitrile for synthetic fibers, intermediates for dye stuff industry and pesticides.

Basic Intermediates:

Paraffins	Methane , propane, butane and higher hydrocarbons
	Ethylene, propylene, butadiene , alcohol, vinyl chloride
Olefins and derivatives	Ethylene, propylene,, butadiene , alcohol, vinyl chloride
Aromatics	Benzene Toluene Ethyl benzene, Xylenes, Naphthalene

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مراحل إنتاج البتروكيماويات

يمر تصنيع البتروكيماويات بعدة مراحل

- مرحلة البتروكيماويات الأساسية

تحويل المواد الخام (ميثان – إيثان – بروبان – البوتان - النافثا) إلى بتروكيماويات أساسية (الميثانول – النشادر – الايثيلين – البروبلين – البوتادايين – البنزين – الزايلين)

- مرحلة البتروكيماويات الوسطية

تمثل حلقة الوصل بين البتروكيماويات الأساسية و معظم البتروكيماويات النهائية مثل (فورمالدهيد – ميلامين - أكسيد الإيثيلين – اثيلين جليكول - ايثانول – أحادي كلوريد الفاينيل - حمض ترفثاليك ....

- مرحلة البتروكيماويات النهائية

مثل بوليمرات (اللدائن – والالياف الصناعية – والمطاط) – الميلامين فورم الدهيد ....

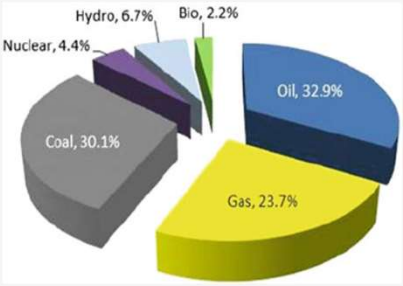
و تمثل البتروكيماويات الاساسية والبتروكيماويات الوسطية والنهائية المواد الخام الأساسية للصناعات التحويلية (الاستهلاكية)

Petroleum and Its Products

Raw Materials For The Chemical Process Industries

Economics:

- Petroleum is an important source of energy.



BP statistical Review of world energy 2015

- Petroleum is a raw material from which we produce lubricants, petrochemicals, construction materials, and thousands of consumer products.
- Large-scale petroleum production began in the late 1850s, and by 1970, oil had overtaken coal as the world's leading source of energy.

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Petroleum and Its Products

Raw Materials For The Chemical Process Industries

Molecular Composition:

- Saturated hydrocarbons can be acyclic paraffins (alkanes) or cyclic paraffins (naphthenes).
- Olefins are very rare in natural petroleum. They are mainly products from thermal cracking in refineries.
- Hydrocarbon Ring Compounds (Naphthenes and Aromatics).
- Heteroatom compounds contain sulfur, nitrogen, oxygen, and trace elements
  - Sulfur is found primarily as H_2S, mercaptans, sulfides, disulfides, thiophenes, benzothiophenes, and polybenzothiophenes. It
  - Nitrogen is present primarily pyrroles, pyridines, quinolines, indoles, and carbazoles.
  - Amides and oxazoles contain both nitrogen and oxygen.
  - Amines are not found in raw crudes.
  - Oxygen compounds include naphthenic acids, carboxylic acids, phenols, cresols, and furans.

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Natural Gas

Raw Materials For The Chemical Process Industries

- Natural gas is a naturally occurring mixture of simple hydrocarbons and nonhydrocarbons that exists as a gas at ordinary pressures and temperatures.
- Natural gas consists principally of methane (CH_4) and ethane (C_2H_6), with fractional amounts of propane (C_3H_8), butane (C_4H_{10}), and other hydrocarbons, pentane (C_5H_{12}) and heavier.
- Natural gas containing the first two of these compounds, hydrogen sulfide and carbon dioxide, is termed "sour" and the contaminants are referred to as "acid" gases.
- Natural gas that contains low enough concentrations of the acid gases to meet sales specifications is termed "sweet."
- Natural gas that contains only traces of other compounds is dry gas.
- If natural gas contains significant amounts of ethane, propane, butanes, and higher hydrocarbons, it is called wet gas.

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Biomass

Raw Materials For The Chemical Process Industries

Wood and Wood Products

Trees provided a source of many products required by early humans such as food, medicine, fuel, and tools.

Chemical Composition of Wood

	Softwood (%)	Hardwood (%)
Component		
Cellulose	42	42
Hemicelluloses		
Xylan	10	20–35
Glucomannan	20	3–4
Lignin	25–35	18–25
Extractives	2–5	2–4

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Raw Materials For The Chemical Process Industries

ROUTES TO PRODUCE CHEMICALS

- Steam Reforming and Partial Oxidation (Synthesis gas ($CO+H_2$ and H_2& N) to produce synthesis gas
- Cracking and Pyrolysis to olefins (C_2H_4,C_3H_6, C_4H_8 and olefins)
- Catalytic Reforming to produce mainly BTX (*mixtures of benzene, toluene, and the three xylene isomers*) from naphtha.
- Dehydrogenation of Paraffin (Paraffin: ethane, paraffin) to produce olefin
- Dehydrogenation (olefin) and alkylation (alkylate) from kerosene for LAB
- Saponification of oil and fats and recovery of chemical from glycerin

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Industrial Catalysis

- The word Organic can be a biological or chemical term, in biology it means anything that is living or has lived.

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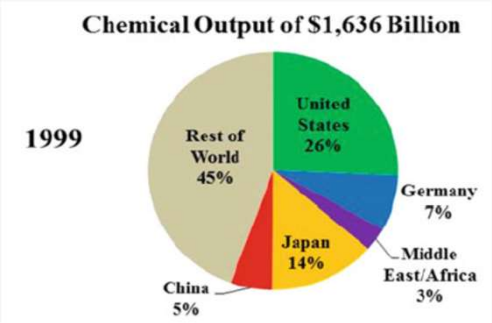
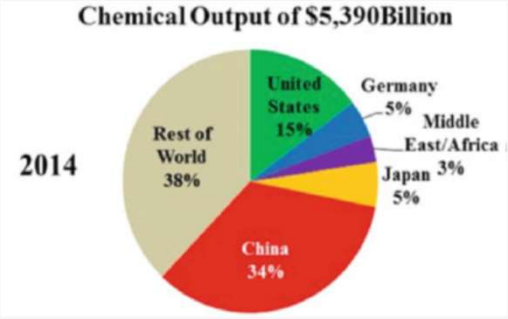
Synthetic Organic Chemicals

- Synthetic organic chemicals are produced by the transformation of carbonaceous feedstocks into functionalized molecules through one or more chemical reactions.
- The molecules produced find use largely as monomers for polymer synthesis of ubiquitous plastics, or as task-specific ingredients for a myriad of applications as divergent as paint leveling agents to food preservatives.





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Chemical Raw Materials and Feedstocks

- An overwhelming majority of the synthetic organic chemicals produced at commercial scale today begin with one of five major types of feedstocks:

1. Light olefins—ethylene and propylene
2. Aromatics—benzene, toluene, xylenes, or BTX
3. C4 hydrocarbons—butanes, butenes, butadiene
4. Kerosene-derived C9–C17 paraffins
5. Synthesis gas—a mixture of carbon monoxide and hydrogen

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Industrial Catalysis: A Practical Guide

- Most products produced in the chemical and petroleum industries utilize catalysts to enhance the rate of reaction and selectivity to desired products.
- Catalysts are also extensively used to minimize the harmful byproduct pollutants in environmental applications.
- Enhanced reaction rates translate to higher production volumes at lower temperatures with smaller reactors and less exotic materials of construction necessary.
- When a highly selective catalyst is used, large volumes of desired products are produced with virtually no undesirable byproducts.

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The Importance of Catalysis

Industrial Catalysis: A Practical Guide

- A catalyst enhances the rate of reactions by lowering the activation energy towards desired products without itself being consumed.
- This permits lower temperatures to be utilized thereby conserving energy, materials of construction while lowering undesired product formation.
- Its ability to accelerate the desired reaction to a specific product referred to selectivity.
- Catalysts are composed of various chemical materials that participate by adsorbing reactants onto its active sites, producing products that rapidly desorb freeing the site for the next catalytic cycle.
- A catalyst increases the reaction rate or activity relative to an un-catalyzed process by providing a less energetic pathway for conversion of reactants to products.

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The Importance of Catalysis

Industrial Catalysis: A Practical Guide

- It is important to keep in mind the importance of catalysts in protecting the environment.
- They are frequently installed in the exhaust ducts of chemical operations to convert toxic volatile organic compounds (VOC) generated during manufacturing into benign products.
- Catalysts also provide the environmental benefit of clean air by abating pollutants generated from stationary and mobile combustion sources.
- In many locations around the industrialized world, coaland gas-fired power plants have special catalysts installed in the ducts to eliminate pollutants dangerous to our health.
- All of this gives the consumer the benefits of readily available high-quality products at reasonable prices.

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How Does a Catalyst Work?

Industrial Catalysis: A Practical Guide

- If no catalyst were present, a higher temperature would be required to initiate the reaction. Higher temperatures often lead to undesirable byproducts and sometimes decomposition of one of the reactants.
- The catalyst is not consumed in the process; it does undergo various chemical changes during the process by interacting with the reactants and products and finally returning to its original state prepared for the next cycle.
- Mechanistically some or all of the reactants adsorb onto active sites where bonds are rapidly made or broken.
- Most catalytic metals and metal oxides are derived from Group VIII of the periodic table.
- Of special importance are Fe, Co, Ni, Rh, Ru, Pd, and Pt, but also of importance are Cu and Ag in Group 1b, V in Group Vb, and Cr and Mo in Group V1b.

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Types of catalytic reactions

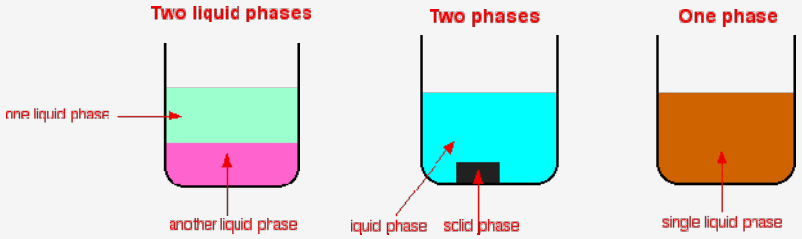
Industrial Catalysis: A Practical Guide

- Catalysts can be divided into two main types
  - heterogeneous and

    the catalyst is in a different phase from the reactants

    Typical examples involve a solid catalyst with the reactants as either liquids or gases.
  - homogeneous.

    the catalyst is in the same phase as the reactants.



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How the heterogeneous catalyst works

Industrial Catalysis: A Practical Guide

- One or more of the reactants are adsorbed on to the surface of the catalyst at active sites.
- *An active site is a part of the surface which is particularly good at adsorbing things and helping them to react.*
- *Desorption simply means that the product molecules break away. This leaves the active site available for a new set of molecules to attach to and react.*

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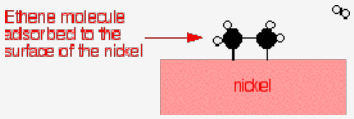
How the heterogeneous catalyst works

Industrial Catalysis: A Practical Guide

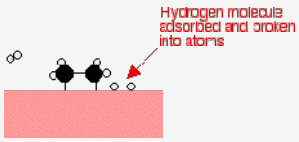
Example; The hydrogenation of a carbon-carbon double bond

$$CH_2{=}CH_2 + H_2 \xrightarrow{Ni} CH_3CH_3$$

- Ethene molecules are adsorbed on the surface of the nickel.
- The double bond between the carbon atoms breaks and the electrons are used to bond it to the nickel surface.



- Hydrogen molecules are also adsorbed on to the surface of the nickel.
- When this happens, the hydrogen molecules are broken into atoms. These can move around on the surface of the nickel.



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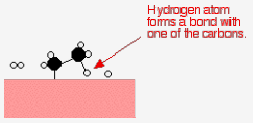
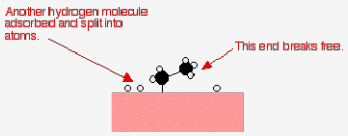
How the heterogeneous catalyst works

Industrial Catalysis: A Practical Guide

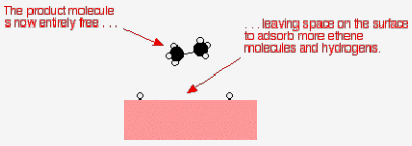
- If a hydrogen atom diffuses close to one of the bonded carbons, the bond between the carbon and the nickel is replaced by one between the carbon and hydrogen.



- That end of the original ethene now breaks free of the surface, and eventually the same thing will happen at the other end.



- As before, one of the hydrogen atoms forms a bond with the carbon, and that end also breaks free. There is now space on the surface of the nickel for new reactant molecules to go through the whole process again.



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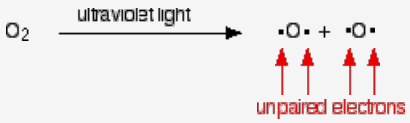
Homogeneous catalysis

Industrial Catalysis: A Practical Guide

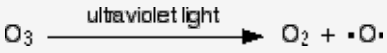
Example; The destruction of atmospheric ozone

- Ozone, O3, is constantly being formed and broken up again in the high atmosphere by the action of ultraviolet light. Ordinary oxygen molecules absorb ultraviolet light and break into individual oxygen atoms. These have unpaired electrons, and are known as free radicals. They are very reactive.



- The oxygen radicals can then combine with ordinary oxygen molecules to make ozone.

- Ozone can also be split up again into ordinary oxygen and an oxygen radical by absorbing ultraviolet light.



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Autocatalysis

Industrial Catalysis: A Practical Guide

- The reaction is catalyzed by one of its products.
- The oxygen radicals can then combine with ordinary oxygen molecules to make ozone.
- Ozone can also be split up again into ordinary oxygen and an oxygen radical by absorbing ultraviolet light.

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