ألمحاضرة ألثالثة

Catalysis in chemical Industry: ألعوامل ألمساعدة في ألصناعات ألكيميائية

Catalyst: is a substance that adds to the chemical reaction to increase the rate of reaction. It is not consumed in the catalyzed reaction but can act repeatedly.

-Often only very small amounts of catalyst are required.

- The global demand for catalysts in 2010 was estimated to about US $29.5 billion

Catalysis: is the process of increasing the rate of a chemical reaction by adding a substance known as a catalyst.

من ألأمثلة أستخدام ألحديد ألمحسن بأكاسيد ألبوتاسيوم في أنتاج ألأمونيا كعامل مساعد من خلال تقيل ظروف ألتفاعل من حرارة و ضغط

$$N2 + H2 \text{ ----------} \rightarrow NH3$$

Illustration توضيح

This reaction proceeds because the reaction products are more stable than the starting material. The uncatalysed reaction is slow. In fact, the reaction of hydrogen with nitrogen is very slow. This reaction is strongly affected by catalysts such as Iron. Upon the addition of a small amount of Iron, the reaction occurs rapidly. This effect is readily seen by the effervescence of Iron. The Iron is not consumed in the reaction, and thus may be

recovered unchanged and re-used indefinitely. Accordingly, Iron catalyses this reaction.

يمكن قياس نشاط ألعامل ألمساعد بوحدات

The SI derived unit for measuring the catalytic activity of a catalyst is the katal, which is moles per second.

و ألتي هي ألمول/ثانية katal وحدة قياس نشاط ألعامل ألمساعد تدعى ألكتل.

و هنالك عدة عمليات صناعية توضف ألعوامل ألمساعدة لأنجازها:

There several industrial processes may be done using catalysts, these processes:

1- **oxidation** processes (organic or inorganic) like oxidation of

2- **hydrogenation** (like hydrogenation of oil in food industry or in petrochemical industry)

RSH + H2 ----Ni -------› RH +H2S

3- **cracking**

4- **halogenations**

There are some compounds called co-catalysts (mixed catalysts). It is necessary for catalysts stability like Al2O3, SiO2, silica

The catalysts may be deactivated by impurities like CO, S, P metals …….etc

Classification

Catalysis may be classified as either homogeneous or heterogeneous:

-A heterogeneous catalysis is one where the reaction components are not in the same phase.

-A homogeneous catalysis is one whose components are dispersed in the same phase (usually gaseous or liquid) as the reactant's molecules.

-Biocatalysis.

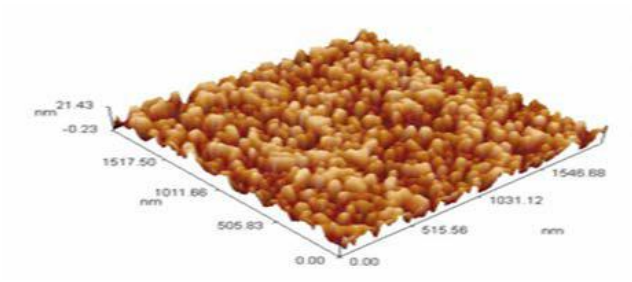
-Photocatalysis

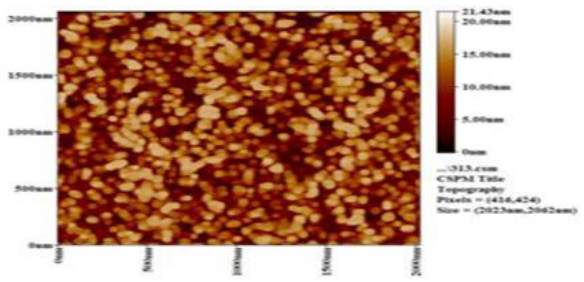
-Organometallic Catalyst

Heterogeneous catalysis

Heterogeneous catalysts act in a different phase than the reactants. Most heterogeneous catalysts are solids that act on substrates in a liquid or gaseous reaction mixture. Important heterogeneous catalysts include zeolites, alumina, higher-order oxides, graphitic carbon, transition metal oxides, metals such as Raney nickel for hydrogenation and vanadium (V) oxide for oxidation of sulfur dioxide into sulfur trioxide by the so-called contact process.

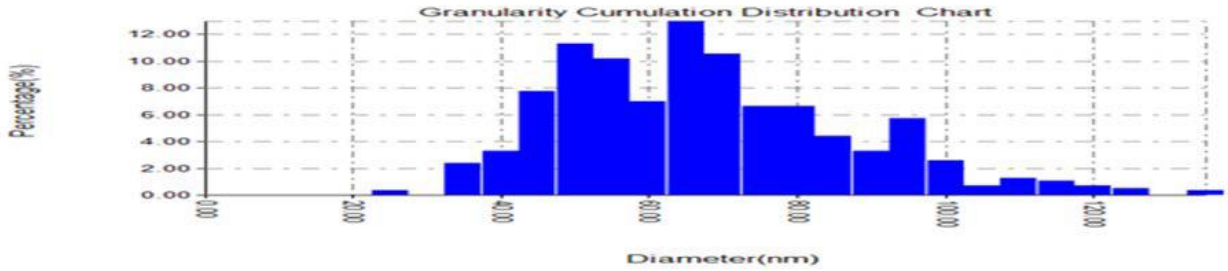
Diverse mechanisms for reactions on surfaces are known, depending on how the adsorption takes place. The total surface area of solid has an important effect on the reaction rate.

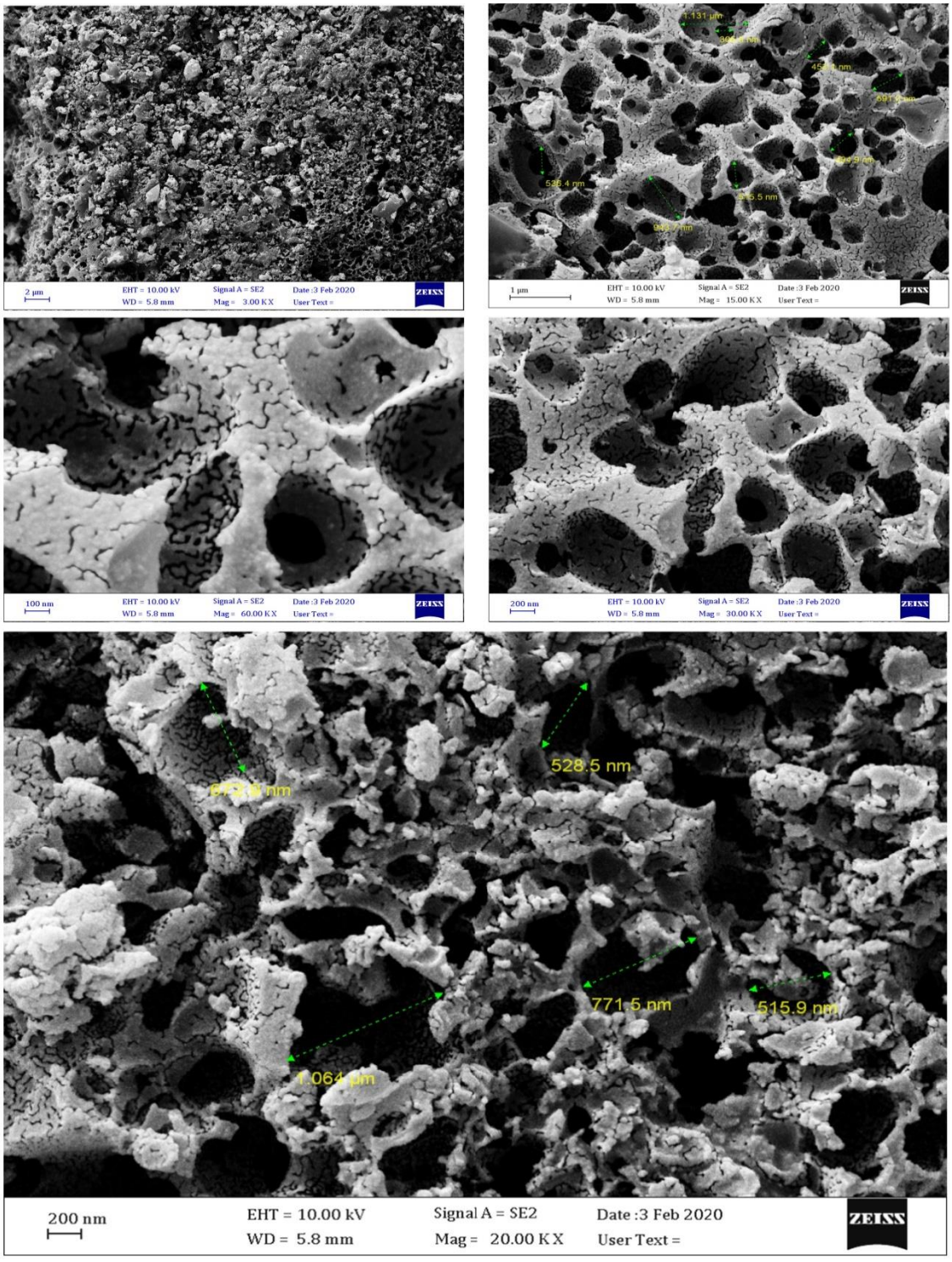




Avg. Diameter:65.18 nm **<=10% Diameter:40.00 nm**

<=50% Diameter:60.00 nm **<=90% Diameter:90.00 nm**





The smaller the catalyst particle size, the larger the surface area for a given mass of particles.

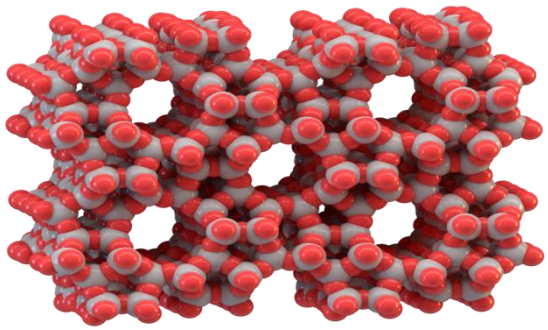
A heterogeneous catalyst has active sites, which are the atoms or crystal faces where the reaction actually occurs. Depending on the mechanism, the active site may be either a planar exposed metal surface, a crystal edge with imperfect metal valence or a complicated combination of the two.

For example, in the Haber process, finely divided iron serves as a catalyst for the synthesis of ammonia from nitrogen and hydrogen. The reacting gases adsorb onto active sites on the iron particles. Once physically adsorbed, the reagents undergo chemisorption that results in dissociation into adsorbed atomic species, and new bonds between the resulting fragments form in part due to their close proximity. In this way the particularly strong triple bond in nitrogen is broken, which would be extremely uncommon in the gas phase due to its high activation energy. Thus, the activation energy of the overall reaction is lowered, and the rate of reaction increases. Another place where a heterogeneous catalyst is applied is in the oxidation of sulfur dioxide on vanadium (V) oxide for the production of sulfuric acid.

$$V_2O_5 + SO_2 \xrightarrow{\text{oxidation}} SO_3$$

In slurry reactions, heterogeneous catalysts can be lost by dissolving.

Many heterogeneous catalysts are in fact nanomaterials.



The microporous molecular structure of the zeolite ZSM-5 is exploited in catalysts used in refineries

Zeolites are extruded as pellets for easy handling in catalytic reactors.

Homogeneous catalysis

Homogeneous catalysts function in the same phase as the reactants. Typically homogeneous catalysts are dissolved in a solvent with the substrates. One example of homogeneous catalysis involves the influence of H+ on the esterification of carboxylic acids, such as the formation of methyl acetate from acetic acid and methanol.

Estimates are that 90% of all commercially produced chemical products involve catalysts at some stage in the process of their manufacture.

Typical mechanism

Catalytic cycle دورة ألعامل ألمساعد

-In general, chemical reactions occur faster in the presence of a catalyst because the catalyst provides an alternative reaction pathway - or mechanism - with lower activation energy than the non-catalyzed mechanism.

-In catalyzed mechanisms, the catalyst usually reacts to form an intermediate, which then regenerates the original catalyst.

Catalysts generally react with one or more reactants to form intermediates that subsequently give the final reaction product, in the process regenerating the catalyst. The following is a typical reaction scheme, where C represents the catalyst, X and Y are reactants, and Z is the product of the reaction of X and Y:

$X + C \rightarrow XC$ ---------- 1

$Y + XC \rightarrow XYC$ ---------- 2

$XYC \rightarrow CZ$ ---------- 3

$CZ \rightarrow C + Z$ ---------- 4

Although the catalyst is consumed by reaction 1, it is subsequently produced by reaction 4. As a catalyst is

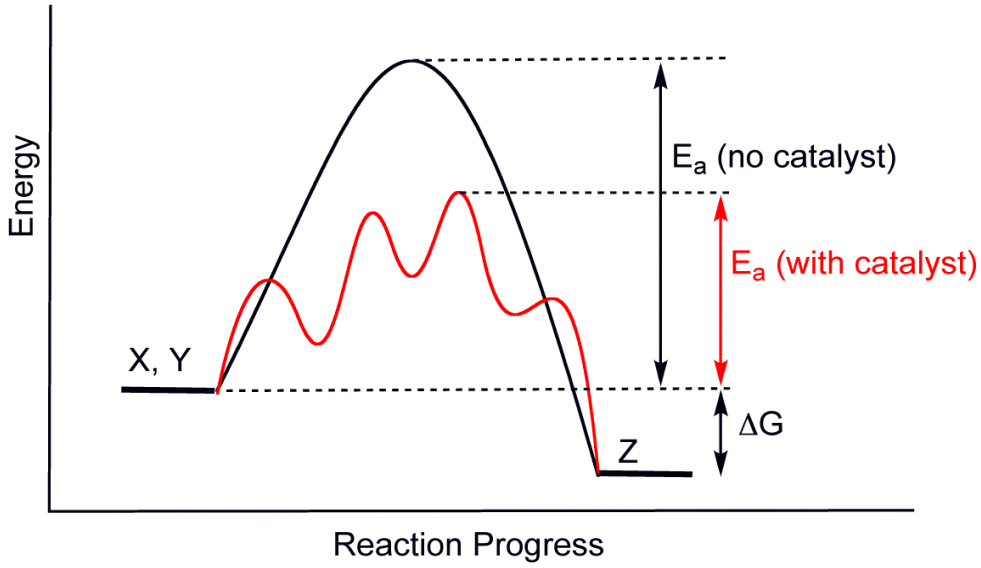
regenerated in a reaction, often only small amounts are needed to increase the rate of the reaction.

Mechanism 1

The effect of catalysts is increasing the reaction rate which can be summarized as:

-that will lead to complex formation in away differ from that complex without cata. and with less activation energy

-So, the No. of molecules which having equal or minimum activation energy is measured so the reaction rate will increase



Generic potential energy diagram showing the effect of a catalyst in a hypothetical exothermic chemical

This interpretation according to the transfer case.

Mechanism 2

But according to collusion theory the role of cata. is decreasing the activation energy which leads to high percent of molecules which have minimum of this low energy that can react and convert to products

Moreover, cata. effect on rate of reaction but doesn't effect on the equilibrium of reaction the reversible reaction

From this fact, the cat. change the rate of reaction but don't effect on the equilibrium

- So it will increase the rate of reaction in both directions in the same value. From this one can conclude that cat. fasten the left reaction i.e. hydrolysis of ester at the same time the cat. fasten the esterification i.e. the reaction of acid and alcohol hydrogenation take place in the same way .

RCOOH + R'OH ‹---------› RCOOR' + H2O

Energy processing

-Petroleum refining makes intensive use of catalysis for alkylation, catalytic cracking (breaking long-chain hydrocarbons into smaller pieces),

-naphtha reforming and steam reforming (conversion of hydrocarbons into synthesis gas).

-Even the exhaust from the burning of fossil fuels is treated via catalysis: Catalytic converters, typically composed of platinum

and rhodium, break down some of the more harmful byproducts of automobile exhaust.

$2\ CO + 2\ NO \rightarrow 2\ CO2 + N2$

مكونات ألعامل ألمساعد

1-**The active materials**:

like Pt or V2O5 or Pd ….etc.

2- **Supporter:**

Heterogeneous catalysts are typically "supported," which means that the catalyst is dispersed on a second material that enhances the effectiveness or minimizes their cost. Supports prevent or reduce agglomeration and sintering small catalyst particles, exposing more surface area, thus catalysts have a higher specific activity (per gram) on a support. Sometimes the support is merely a surface on which the catalyst is spread to increase the surface area. Supports are porous materials with a high surface area, most commonly alumina, zeolites or various kinds of activated carbon. Specialized supports include silicon dioxide, titanium dioxide, calcium carbonate, and barium sulfate.

3-**Promoters**:

are substances that increase the catalytic activity, even though they are not catalysts by themselves. They can aid the dispersion of the catalytic material or bind to reagents.

4- **Inhibitors:**

are sometimes referred to as "negative catalysts" since they decrease the reaction rate.

However, we can get mixed catalytic systems containing several components with large porous surface area by the methods:

1- Mixed and press grind component with each other on shape of granules in different sizes

2- Heating the mixture

3- Using method of precipitation of cata. from solvents

However, using catalyst in industry required (contact – catalysis) special designed in reactors.

Feature of catalysts:

1- High efficiency and selectivity

2- Large surface area

3- Long life and high stability

4- Easy regeneration