Homogeneous and Heterogeneous Catalysis:Teachings of the Thermal Energy and Power Engineering Course

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***Abstract*—**It is usually difficult for students to understand some basic theories in learning thermal energy and power engineering course. A new teaching method was proposed that we should introduce the comparison research method of those theories to help them being understood. "Homogeneous and heterogeneous catalysis" teaching is analyzed as an example by comparison research method.

***Keywords*—**Homogeneous catalysis, heterogeneous catalysis, thermal energy and power engineering, teaching method, comparison research method.

I. INTRODUCTION

CATALYSTS are chemicalcompounds that can increase the rate of a reaction by lowering the activation energy required to reach the transition state. Unlike reactants, a catalyst is not consumed as part of the reaction process.

Catalysts can be divided into two types depending on the reaction phase that they occupy: homogeneous and heterogeneous. Homogeneous catalysts are those that occupy the same phase as the reaction mixture (typically liquid or gas), while heterogeneous catalysts occupy a different phase. In general, heterogeneous catalysts are solid compounds that are mixed with liquid or gas reaction mixtures. Typical examples of heterogeneous catalysis involve the absorption of ethylene onto a solid catalyst followed by hydrogenation of the double bond to yield ethane.

In general, heterogeneous catalysis requires the diffusion of one or more reactants to the catalyst surface, followed by the absorption onto a solid catalyst. The use of heterogeneous catalysts has both advantages and disadvantages. On one hand, diffusion to a binding site on a solid catalyst can often be the rate-limiting step in a reaction catalyzed by a heterogeneous catalyst. In addition, the available surface area of the heterogeneous catalyst will also affect the reaction rate, as it will dictate and potentially limit the number of reaction sites that are available. On the other hand, heterogeneous catalysis does have a number of benefits. Heterogeneous catalysts can be separated from a reaction mixture in a straightforward manner, such as by filtration. In this way, expensive catalysts can be easily and effectively recovered, which is an important consideration for industrial manufacturing processes.

II. HOMOGENEOUS CATALYSIS

In chemistry, homogeneous catalysis is a sequence of reactions that involve a catalyst in the same phase as the

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reactants. Phases here refer to solid, liquid and gas. Most commonly, a homogeneous catalyst is codissolved in a solvent with the reactants.

A. Acid Catalysis

An acid is a chemical substance whose aqueous solutions are characterized by a sour taste, the ability to turn blue litmus red, and the ability to react with bases and certain metals (like calcium) to form salts. Aqueous solutions of acids have a pH of less than 7. A lower pH means a higher acidity, and thus a higher concentration of positive hydrogen ions in the solution. Chemicals or substances having the property of an acid are said to be acidic.

The proton is the most pervasive homogeneous catalyst because water is the most common solvent [1]. Water forms protons by the process of self-ionization of water. In an illustrative case, acids accelerate (catalyze) the hydrolysis of esters:

$$CH_3CO_2CH_3 + H_2O = CH_3CO_2H + CH_3OH$$
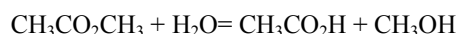
In the absence of acids, aqueous solutions of most esters do not hydrolyze at practical rates.

B. Organometallic Chemistry

Organometallic chemistry is the study of chemical compounds containing at least one bond between a carbon atom of an organic compound and a metal. Organometallic chemistry combines aspects of inorganic chemistry and organic chemistry. Organometallic compounds are widely used in homogeneous catalysis.

Organometallic compounds are distinguished by the prefix "organo-" e.g. organopalladium compounds. Examples of such organometallic compounds include all Gilman reagents, which contain lithium and copper. Tetracarbonylnickel and ferrocene are examples of organometallic compounds containing transition metals. Other examples include organomagnesium compounds like iodo(methyl)magnesium (MeMgI), diethylmagnesium (Et$_2$Mg), and all Grignard reagents; organolithium compounds such as n-butyllithium (n-BuLi), organozinc compounds such as diethylzinc (Et$_2$Zn) and chloro(ethoxycarbonylmethyl)zinc (ClZnCH$_2$C(=O)OEt); and organocopper compounds such as lithium dimethylcuprate (Li$^+$[CuMe2]$^-$).

Processes that utilize soluble organometallic compounds as catalysts fall under the category of homogeneous catalysis, as opposed to processes that use bulk metal or metal on a solid support, which are examples of heterogeneous catalysis. Some well-known examples of homogeneous catalysis include

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hydroformylation and transfer hydrogenation, as well as certain kinds of Ziegler-Natta polymerization and hydrogenation [2]. Homogeneous catalysts has also been used in a variety of industrial processes such as the Wacker process Acetaldehyde (conversion of ethylene to acetaldehyde) as well as the Monsanto process and the Cativa process for the conversion of MeOH and CO to acetic acid.

Many non-organometallic complexes are also widely used in catalysis, e.g. for the production of terephthalic acid from xylene.

C. Other Forms of Homogeneous Catalysis

Enzymes are homogeneous catalysts that are essential for life but are also harnessed for industrial processes. A well-studied example is carbonic anhydrase, which catalyzes the release of CO_2 into the lungs from the blood stream.

D. Contrast with Heterogeneous Catalysis

Homogeneous catalysis differs from heterogeneous catalysis in that the catalyst is in a different phase than the reactants. One example of heterogeneous catalysis is the petrochemical alkylation process, where the liquid reactants are immiscible with a solution containing the catalyst. Heterogeneous catalysis offers the advantage that products are readily separated from the catalyst, and heterogeneous catalysts are often more stable and degrade much slower than homogeneous catalysts. However, heterogeneous catalysts are difficult to study, so their reaction mechanisms are often unknown [3].

Enzymes possess properties of both homogeneous and heterogeneous catalysts. As such, they are usually regarded as a third, separate category of catalyst.

III. HETEROGENEOUS CATALYSIS

In chemistry, heterogeneous catalysis refers to the form of catalysis where the phase of the catalyst differs from that of the reactants. Phases here refer not only to solid, liquid and gas, but also immiscible liquids, e.g. oil and water. The great majority of practical heterogeneous catalysts are solids and the great majority of reactants are gases or liquids [4]. Heterogeneous catalysis is of paramount importance in many areas of the chemical and energy industries. Heterogeneous catalysis has attracted Nobel prizes for Fritz Haber and Carl Bosch in 1918, Irving Langmuir in 1932, and Gerhard Ertl in 2007[5].

A. Adsorption

Adsorption is commonly an essential first step in heterogeneous catalysis. Adsorption is when a molecule in the gas phase or in solution binds to atoms on the solid or liquid surface. The molecule that is binding is called the adsorbate, and the surface to which it binds is the adsorbent. The process of the adsorbate binding to the adsorbent is called adsorption. The reverse of this process (the adsorbate splitting from adsorbent) is called desorption. In terms of catalyst support, the catalyst is the adsorbate and the support is the adsorbent.

Two types of adsorption are recognized in heterogeneous catalysis, although many processes fall into an ambiguous range between the two extremes. In the first type,

physisorption, induces only small changes to the electronic structure of the adsorbate. Typical energies for physisorption are from 2 to 10 kcal/mol. The second type is chemisorption, in which the adsorbate is strongly perturbed, often with bond-breaking. Energies for typical chemisorptions range from 15 to 100 kcal/mol.

For physisorption, adsorbate is attracted to the surface atoms by van der Waals forces. A mathematical model for physisorption was developed by London to predict the energies of basic physisorption of non-polar molecules. The analysis of physisorption for polar or ionic species is more complex.

Chemisorption results in the sharing of electrons between the adsorbate and the adsorbent. Chemisorption is traditionally described by the Lennard-Jones potential, which considers various cases, two of which are.

Molecular adsorption: the adsorbate remains intact. An example is alkene binding by platinum.

Dissociative adsorption: one or more bonds break concomitantly with adsorption. In this case the barrier to dissociation affects the rate of adsorption. An example of dissociative adsorptionis the binding of H_2, where the H-H bond is broken upon adsorption [6].

B. Surface Reactions

With catalyst supports, the reaction that occurs often occurs on the surface of either the catalyst or the support. In terms of surface reactions there are three mechanisms.

Langmuir-Hinshelwood mechanism: The two molecules A and B both adsorb to the surface. While adsorbed to the surface, the A and B "meet," bond, and then the new molecule A-B desorbs.

Rideal-Eley mechanism: One of the two molecules, A, adsorbs to the surface. The second molecule, B, meets A on the surface, having never adsorbed to the surface, and they react and bind. Then the newly formed A-B desorbs.

Precursor mechanism: One of the two molecules, A, is adsorbed on the surface. The second molecule, B, collides with the surface, forming a mobile precursor state. The molecule B then collides with A on the surface, they react, bind and the new molecule desorbs.

Any surface reaction can be described as following one of these mechanisms, or some combination of these mechanisms. In addition, all of these above mechanisms can occur in reverse. In general, the pathway for a reaction on a surface is as follows. First the reactants adsorb onto the surface. Through a series of bonds being formed and being broken, adsorbed intermediates are produced and destroyed. Then the final product(s) is produced and it desorbs from the solid. Most metal surface reaction occurs by chain propagation [6].

C. Concepts

In heterogeneous catalysis, the reactants diffuse to the catalyst surface and adsorb onto it, via the formation of chemical bonds. After reaction, the products desorb from the surface and diffuse away. Understanding the transport phenomena and surface chemistry such as dispersion is important. If diffusion rates are not taken into account, the

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reaction rates for various reactions on surfaces depend solely on the rate constants and reactant concentrations. For solid heterogeneous catalysts, the surface area of the catalyst is critical since it determines the availability of catalytic sites. Surface areas can be large, for example some mesoporous silicates have areas of 1000 m^2/g. The most common approach to maximizing surface area is by the use of catalyst supports, which are the materials over which the catalysts are spread.

D. Classes of Heterogeneous Catalysts

Although the majority of heterogeneous catalysts are solids, many variations exist. Reacting phases: solid + gas, solid + solution, and immiscible liquid phases.

IV. EXAMPLES OF THE HETEROGENEOUS CATALYSIS

Many examples exist; the table emphasizes large-scale industrial processes [7], although diverse examples are known.

A. Sulfuric Acid Synthesis

Sulfuric acid (alternative spelling sulphuric acid) is a highly corrosive strong mineral acid with the molecular formula H2SO4. It is a pungent-ethereal, colorless to slightly yellow viscous liquid which is soluble in water at all concentrations. Sometimes, it is dyed dark brown during production to alert people to its hazards. The historical name of this acid is oil of vitriol.

Sulfuric acid is a diprotic acid and shows different properties depending upon its concentration. Its corrosiveness on other materials, like metals, living tissues (e.g. skin and flesh) or even stones, can be mainly ascribed to its strong acidic nature and, if concentrated, strong dehydrating and oxidizing property. Sulfuric acid at a high concentration can cause very serious damage upon contact, as it not only causes chemical burns via hydrolysis, but also secondary thermal burns via dehydration. It burns the cornea and can lead to permanent blindness if splashed onto eyes. Accordingly, safety precautions should be strictly observed when handling it. Moreover, it is hygroscopic, readily absorbing water vapour from the air.

The contact process is the current method of producing sulfuric acid in the high concentrations needed for industrial processes. Platinum was formerly employed as a catalyst for the reaction, but as it is susceptible to poisoning by arsenic impurities in the sulfur feedstock, vanadium (V) oxide (V_2O_5) is now preferred.

B. Ammonia Synthesis

Ammonia, or azane, is a compound of nitrogen and hydrogen with the formula NH_3. It is a colourless gas with a characteristic pungent smell. Ammonia contributes significantly to the nutritional needs of terrestrial organisms by serving as a precursor to food and fertilizers. Ammonia, either directly or indirectly, is also a building-block for the synthesis of many pharmaceuticals, or is used in many commercial cleaning products. Although in wide use, ammonia is both caustic and hazardous. The global industrial production of ammonia for 2012 was anticipated to be 198,000,000 tonnes (195,000,000 long tons; 218,000,000 short tons), a 35% increase over the estimated 2006 global output of 146,500,000 tonnes (144,200,000 long tons; 161,500,000 short tons).

Ammonia is found in trace quantities in the atmosphere, being produced from the putrefaction (decay process) of nitrogenous animal and vegetable matter. Ammonia and ammonium salts are also found in small quantities in rainwater, whereas ammonium chloride (sal-ammoniac), and ammonium sulfate are found in volcanic districts; crystals of ammonium bicarbonate have been found in Patagonian guano. The kidneys secrete NH3 to neutralize excess acid. Ammonium salts are found distributed through fertile soil and in seawater. Ammonia is also found throughout the Solar System on Pluto, Mars, Jupiter, Saturn, Uranus, and Neptune. Substances containing ammonia, or those that are similar to it, are called ammoniacal.

The Haber process, also called the Haber-Bosch process, is the industrial implementation of the reaction of nitrogen gas and hydrogen gas. It is the main industrial procedure to produce ammonia:

$$N_2 + 3\,H_2 \rightarrow 2\,NH_3 \quad (\Delta H = -92.4 \text{ kJ·mol}^{-1})$$
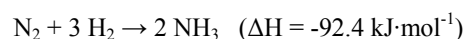
Nitrogen is a strong limiting nutrient in plant growth. Carbon and oxygen are also critical, but are easily obtained by plants from soil and air. Even though air is 78% nitrogen, atmospheric nitrogen is nutritionally unavailable because nitrogen molecules are held together by strong triple bonds. Nitrogen must be 'fixed', i.e. converted into some bioavailable form, through natural or man-made processes. It was not until the early 20th century that Fritz Haber developed the first practical process to convert atmospheric nitrogen to ammonia, which is nutritionally available. Prior to the discovery of the Haber process, ammonia had been difficult to produce on an industrial scale. Nitrogen fixation was already being done on an industrial scale using the Birkeland-Eyde process, but this is very energy-inefficient.

Fertilizer generated from ammonia produced by the Haber process is estimated to be responsible for sustaining one-third of the Earth's population. It is estimated that half of the protein within human beings is made of nitrogen that was originally fixed by this process; the remainder was produced by nitrogen fixing bacteria and archaea.

C. Nitric Acid Synthesis

Nitric acid (HNO_3), also known as aqua fortis and spirit of niter, is a highly corrosive mineral acid. The pure compound is colorless, but older samples tend to acquire a yellow cast due to decomposition into oxides of nitrogen and water. Most commercially available nitric acid has a concentration of 68%. When the solution contains more than 86% HNO_3, it is referred to as fuming nitric acid. Depending on the amount of nitrogen dioxide present, fuming nitric acid is further characterized as white fuming nitric acid or red fuming nitric acid, at concentrations above 95%.

Commercially available nitric acid is an azeotrope with water at a concentration of 68% HNO3, which is the ordinary concentrated nitric acid of commerce. This solution has a boiling temperature of 120.5 °C at 1 atm. Two solid hydrates

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are known; the monohydrate ($HNO_3 \cdot H_2O$) and the trihydrate ($HNO_3 \cdot 3H_2O$).

Nitric acid of commercial interest usually consists of the maximum boiling azeotrope of nitric acid and water, which is approximately 68% HNO_3, (approx. 15 molar). This is considered concentrated or technical grade, while reagent grades are specified at 70% HNO_3. The density of concentrated nitric acid is 1.42 g/mL. An older density scale is occasionally seen, with concentrated nitric acid specified as 42° Baumé.

The Ostwald process is a chemical process for making nitric acid (HNO_3). Wilhelm Ostwald developed the process, and he patented it in 1902. The Ostwald process is a mainstay of the modern chemical industry, and it provides the main raw material for the most common type of fertilizer production. Historically and practically, the Ostwald process is closely associated with the Haber process, which provides the requisite raw material, ammonia (NH_3).

D.Hydrogen Cyanide Synthesis

Hydrogen cyanide (HCN), sometimes called prussic acid, is an inorganic compound with the chemical formula HCN. It is a colorless, extremely poisonous liquid that boils slightly above room temperature, at 25.6 °C (78.1 °F) [8]. HCN is produced on an industrial scale and is a highly valuable precursor to many chemical compounds ranging from polymers to pharmaceuticals.

The Andrussow process is an industrial process for the production of hydrogen cyanide from methane and ammonia in the presence of oxygen and a platinum catalyst.

$$CH_4 + NH_3 + 1.5\ O_2 \rightarrow HCN + 3\ H_2O$$
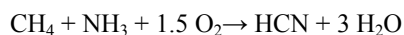
V. CONCLUSION

We often explain theory concepts to students in the course of teaching activities. It is insufficient to demonstrate one theory by only its own contents. Above all, we should further give the comparison researchmethod of the theory. By the comparison researchmethod, students will not only understand the theory more easily but also learn the difference from each other. It seems especially more and more important to use the comparison researchmethod in advocating education today than ever before.

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