CHAPTER II

THEORY AND LITERATURE REVIEWS

2.1 Cyclohexane oxidation [4]

The selective oxidation of cyclohexane produces an important KA-oil (a mixture of cyclohexanone and cyclohexanol) intermediate in the petroleum industrial chemistry. Such oil can be used for the production of adipic acid and caprolactam, which are key materials for manufacturing 6,6-nylon and 6-nylon, respectively Modern industrial methods usually require high pressure and temperature when using soluble cobalt as catalyst, which has led to the realization of high selectivity (about 80%) for the sum of cyclohexanone and cyclohexanol only at a low conversion (1–4 mol%), since the cyclohexanone and cyclohexanol are substantially more reactive than the cyclohexane reactant. Thus, it is difficult to receive high conversion and selectivity simultaneously under mild conditions.

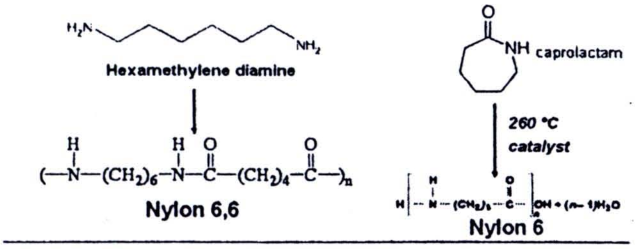


Figure 2.1 Cyclohexane to nylon 6,6 and nylon 6.

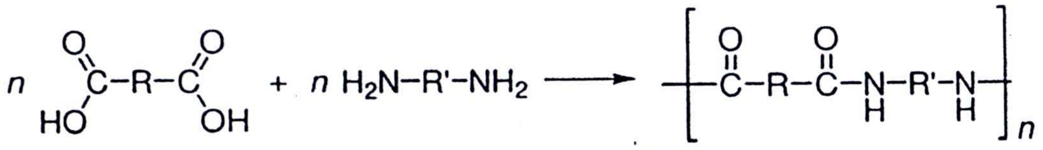
2.2 Adipic acid [5]

Adipic acid (also called hexanedioic acid) is a white, crystalline compound of C6 straight-chain dicarboxylic acid; slightly soluble in water and soluble in alcohol and acetone. Almost all of the commercial adipic acid is produced from cyclohexane through two sequent oxidation processes. The first oxidation is the reacting of cyclohexane with oxygen in the presents of cobalt or manganese catalysts at a temperature of 150 - 160 °C, which produce cyclohexanol and cyclohexanone. Then, the intermediates are further reacted with nitric acid and air with a catalyst (copper or vanadium) or without nitric acid. Adipic acid consumption is linked almost 90% to nylon production by the polycondensation with hexamethylenediamine. Adipic acid is also used in manufacturing plasticizers and lubricants components. Its derivatives, acyl halides, anhydrides, esters, amides and nitriles, are used in making target products such as flavoring agents, pesticides, dyes, textile treatment agents, fungicides, and pharmaceuticals.

2.3 Nylons [6]

Nylons are condensation copolymers formed by reacting equal parts of a diamine and a dicarboxylic acid, so that peptide bonds form at both ends of each monomer in a process analogous to polypeptide biopolymers. Chemical elements included are carbon, hydrogen, nitrogen, and oxygen. The numerical suffix specifies the numbers of carbons donated by the monomers; the diamine first and the diacid second. The most common variant is nylon 6-6 which refers to the fact that the diamine (hexamethylene diamine) and the diacid (adipic acid) each donate 6 carbons to the polymer chain. As with other regular copolymers like polyesters and polyurethanes, the "repeating unit" consists of one of each monomer, so that they alternate in the chain. Since each monomer in this copolymer has the same reactive group on both ends, the direction of the amide bond reverses between each monomer, unlike natural polyamide proteins which have overall directionality: DuPont patented nylon 6,6, so in order to compete, other companies (particularly the German BASF) developed the homopolymer nylon 6, a condensation polymer, but formed by a ring-opening polymerization (alternatively made by polymerizing aminocaproic acid). The peptide bond within the caprolactam is broken with the exposed active groups on each side being incorporated into two new bonds as the monomer becomes part of the polymer backbone. In this case, all amide bonds lie in the same direction, but the properties of nylon 6 are sometimes indistinguishable from those of nylon 6,6 except for melt temperature (N6 is lower) and some fiber properties in products like carpets and textiles.

The general reaction is:



Scheme 2.1 Synthesis of Nylon.

2.4 Homogeneous and heterogeneous catalysts

Homogeneous catalysts are often more selective, more active, and more reproducible, but are generally more difficult to remove after the reaction. In this case, complicated processes such as distillation, liquid-liquid extraction and ion exchange must often be used.

Heterogeneous catalysts can be easily separated from the reaction mixture without any solvent, and show easy regeneration and have a less corrosive character, leading to safer, cheaper and more environment-friendly operation.

Table 2.1 Comparison of homogeneous and heterogeneous catalysts

	Homogeneous	Heterogeneous
Active centers	all metal atoms	only surface atoms
Concentration	low	high
Selectivity	high	lower
Diffusion problems	practically absent	present
Reaction condition	mild (50-200°C)	severe (often> 250°C)
Application	limited	wide
Activity loss	irreversible reaction with products (cluster formation); poisoning	sintering of the metal crystallites; poisoning
Catalyst properties		
Structure/stoichiometry	defined	undefined
Modification possibilities	high	low
Thermal stability	low	high

Table 2.1 Comparison of homogeneous and heterogeneous catalysts(Cont.)

	Homogeneous	Heterogeneous
Catalyst separation	sometimes laborious (chemical decomposition, distillation, extraction)	fixed-bed: unnecessary suspension: filtration
Catalyst recycling	possible	unnecessary
Cost of catalyst losses	high	low

2.4.1 Polyoxometalate [7]

Among the solid acid catalysts, polyoxometalates (POMs) are more efficient catalyst and have many advantages over conventional acid catalysts. The applications of polyoxometalates are based on their unique properties, including size, mass, electron and proton transfer/storage abilities, thermal stability, liability of lattice oxygen and high Brønsted acidity of the corresponding acids. They have long been used in analytical chemistry, in many pharmaceuticals and in medicinal chemistry. The catalytic function of polyoxometalates is used in solution as well as in the solid state, as acid and oxidation catalysts.

The strong acidity of POMs is caused by two main factors: 1) The dispersion of the negative charge over many atoms of the polyanions and 2) The negative charge is less distributed over the outer surface of the polyanions owing to the double-bond character of the M=O bond, which polarizes the negative charge of O to M.

There are a large number of different POMs, but the most well known and studied are the Keggin type due to their easy preparation, relatively high redox and acid properties, and thermal stability. The basic structural unit of these compounds is the Keggin anion $[X^{n+}M_{12}O^{40}]^{n-8}$ (Fig. 2.1), which consists of a central tetrahedron (X: B^{3+}, Si^{4+}, P^{5+}, etc.) surrounded by twelve edge-sharing metal-oxygen (M: Mo^{6+}, W^{6+}) octahedron.

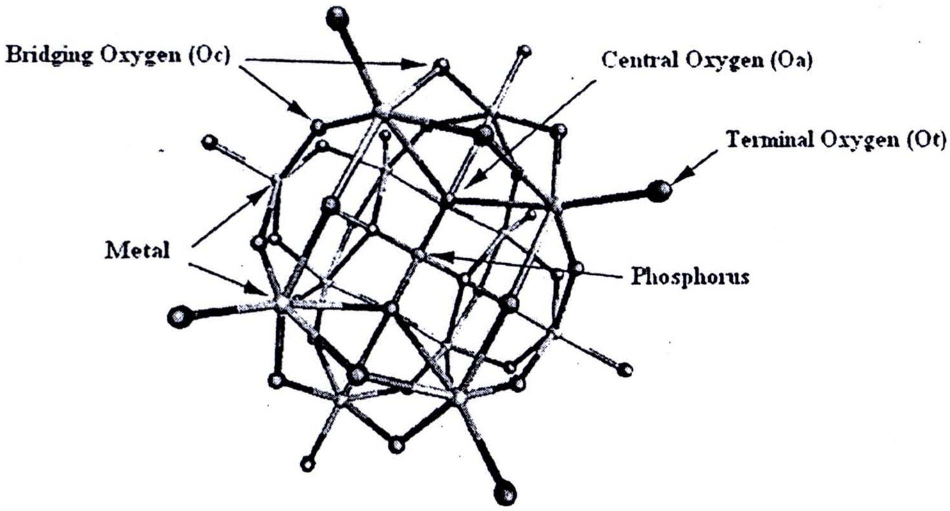


Figure 2.2 Primary structure of the polyoxometalate (Keggin structure).

2.5 Mesoporous materials

In 1992, researchers at Mobil Corporation discovered the M41S family of silicate/aluminosiligate mesoporous molecular sieves with exceptionally large uniform pore structures. The temperature agent used is no longer a single, solvated organic molecule or metal ion, but rather a self-assembled surfactant molecular array as suggested initially. Three different mesophase in this family have been identified, i.e., lamellar hexagonal, and cubic phase. MCM-41[8] has a hexagonally packed array of cylindrical pores. The structure of MCM-48[9] has a three-dimensional,cubic-ordered pore structure and MCM-50[10] contain a lamellar structure as illustrated in Figure 2.3.

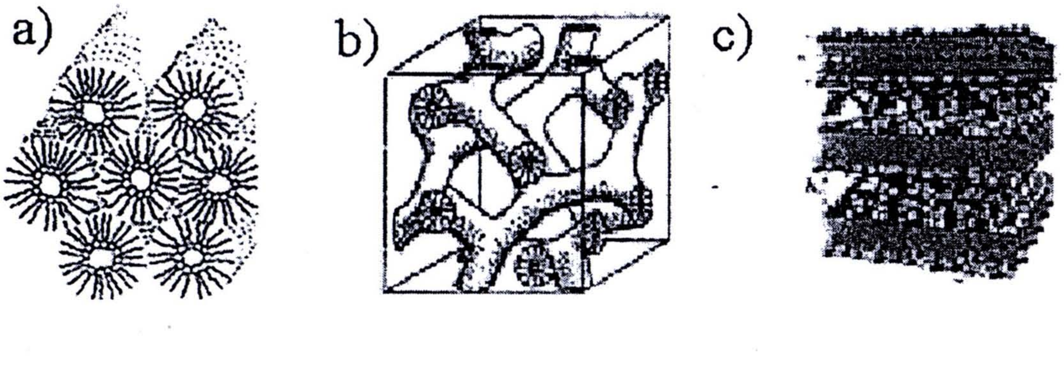


Figure 2.3 A presentation of three inorganic-surfactant mesostructures:
(a) the hexagonal phase, (b) the cubic phase, and (c) the lamellar phase.

2.5.1 MCM-41[11]

MCM-41 (Mobil Composition of Matter)-41, a member of the extensive family of mesoporous molecular sieves, displays an ordered structure with uniform mesoporous arranged into a hexagonal, honeycomb-like lattice as show in Figure2.4. These materials possess large surface area, up to more than 1000 m^2g^{-1} Moreover, the pore diameter of these materials can be controlled within mesoporous range between 1.5 to 20 nm by adjusting the synthesis conditions and/or by employing surfactants with different chain lengths in their preparation. The high thermal and hydrothermal stability, uniform size and shape of the pores, large surface areas and, hydrophobicity and acidity of these materials make them of interest as sorbents and solid support in catalysis.

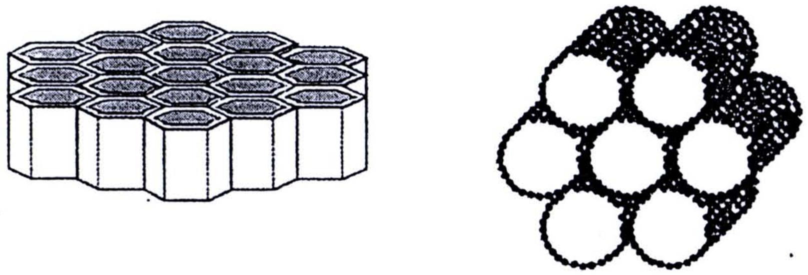


Figure 2.4 Hexagonal packing of uni-dimensional cylindrical pores.

2.6 Hydrogen peroxide, H_2O_2

Hydrogen peroxide is an effective oxidant that could be used in many industrial processes because the only by-product of oxidation using hydrogen peroxide is water. It is commercially available in aqueous solutions of 30% or 90% concentration. The 30% hydrogen peroxide is a colorless liquid (*d* 1.110) and it is stabilized against decomposition, which occurs in the presence of traces of iron, copper, aluminum, platinum, and other transition metals. The 30% hydrogen peroxide does not mix with nonpolar organic compounds. When formic or acetic acid is used, the reacting species is the corresponding peroxy acid. Under such conditions, the products of oxidation by hydrogen peroxide resemble those obtained with peroxy acid.

2.7 Literature reviews

2.7.1 Homogeneous catalysis

In 1992 Barton *et al.* [12] reported the use of $Cu(OAc)_2.6H_2O$ and $FeCl_3.6H_2O$ as catalyst in GoChAgg system. GoChAgg system is the homogeneous oxidation by $Cu(II)$-H_2O_2 in pyridine-acetic acid. Reactivity, selectivity and mechanistic study of system by using various cycloalkanes such as cyclohexane, cycloheptane, adamantine as substrate were thoroughly examined. The mechanism proposed was involved non-radical pathway.

In 1995 Craig L *et al.* [13] studied the redox characteristics of the polyoxometalates. The redox potentials depend on negative charge density and elemental composition. The polyoxometalate ions in order of decreasing redox potentials are V(V) (most oxidizing) > Mo(VI) > W(VI) (least oxidizing).

In 1996, Chavez *et al.* [14] reported the use of Co(III) alkyl peroxide to catalyze in oxidation of cyclohexane to cyclohexanone and cyclohexanol by using tert-BuOOH as oxidant. The selectivity of the reaction was low but the time required for reaction was short.

In 1997 Noritaka *et al.* [15] studied oxidation of cyclohexane to the corresponding alcohols and ketones with molecular oxygen catalyzed by the $Fe_{3-x}Ni_x$-substituted Keggin-type heteropolyanion, $[PW_9O_{37}(Fe_{3-x}Ni_x.(OAc))]^{(9+x)-}$ (x = 1). Its catalytic activities of $[PW_9O_{37}\{Fe_{3-x}Ni_x.(OAc)3\}]^{(9+x)-}$ was compared with mono-transition-metal substituted heteropolytungstates and other compounds having oxo-bridged tri-transition-metal sites. The reaction was carried out without any solvent, air 1 atm , at 82 °C for 48 h. The result showed that $[PW_9O_{37}\{Fe_2Ni_1.(OAc)_3\}]^{(10)-}$ gave 0.36% conversion and 83% selectivity of cyclohexanone.

In 2001 Suss-Fink *et al.* [16] studied oxidation of alkanes (cyclooctane, *n*-octane, adamantane, ethane) by hydrogen peroxide in acetonitrile using tetra-*n*-butylammonium salts of the vanadium-containing polyphosphomolybdates $[PMo_{11}VO_{40}]^{4-}$ and $[PMo_6V_5O_{39}]^{12-}$ catalysts. The oxidation of alkanes gave rise to the corresponding alkyl hydroperoxides as the main products, which slowly decomposed to produce the corresponding ketones (aldehydes) and alcohols. The reaction in acetic acid and water is much less efficient. The oxidation of cyclooctane at 60°C in acetonitrile gives within 9 h oxygenates with turnover numbers >1000 and yields >30%. Pyrazine-2-carboxylic acid added as co-catalyst accelerates the reaction but does not enhance the product yield.

In 2001 Mizumo *et al.* [17] compared the catalytic activity of tetrabutylammonium salts of mono-, di- and tri-iron-substituted. Best results were obtained with the diiron species and the main products were cyclohexanone and cyclohexanol. Keggin-type heteropolytungstates $[PW_{11}O_{39}]^{7-}$ and $[PW_{11}M(L)O_{39}].^{(7-m)-}$ (where M^{m+} = Co, Mn or Ni and L = H_2O or CH_3CN) as catalysts in cyclohexane oxidation with H_2O_2. The polyanions $[PW_{11}O_{39}]^{7-}$ and $[PW_{11}Fe(H_2O)O_{39}]^{4-}$ showed higher catalytic activity. With iron species, a conversion of 76% .

In 2004 Salete *et al.* [18] synthesized tetrabutylammonium salts of the Keggin-type polyoxotungstates $[XW_{12}O_{40}]^{n-}$, $[XW_{11}O_{39}]^{(n+4)-}$, $[XW_{11}VO_{40}]^{m-}$ and $[XW_{11}M^{III}(H_2O)O_{39}]^{p-}$, X = P or Si and M = Fe or Mn. These were used for the oxidation of cyclooctane with hydrogen peroxide in acetonitrile. High turnover numbers and selectivity for cyclooctyl hydroperoxide were obtained. They got 13-96% cyclooctane conversion after 9 h. The tungstosilicates were less active than tungstophosphates but presented higher selectivity for cyclooctyl hydroperoxide. Excess of hydrogen peroxide afforded higher selectivity for cyclooctyl hydroperoxide.

In 2004 Kholdeeva *et al.* [1] reported the aerobic oxidation of isobutyraldehyde with $[(n\text{-}C_4H_9)_4N]_4H[PW_{11}CoO_{39}]$, and $[(n\text{-}C_4H_9)_4N]_5[PW_{11}CoO_{39}]$. The reaction was carried in acetonitrile, air 1 atm at 20°C for 6 h. The results found that $[(n\text{-}C_4H_9)_4N]_4H[PW_{11}CoO_{39}]$ gave higher activity than $[(n\text{-}C_4H_9)_4N]_5[PW_{11}CoO_{39}]$ (94 and 71% conversion) with 54% selectivity of isobutyric acid. From the result indicated that the presence of proton is important for the activity of Co-POMs in isobutyraldehyde oxidation.

In 2008, Mirkhani, *et al.* [19] published the oxidation of alkanes (cyclohexane, cyclooctane and ethylbenzene) with H_2O_2 using Fe^{3+}(salen)Cl and M(salen)-C, where M = Fe, Co, Ni and Mn at 80°C for 5 h in CH_3CN. It was found that Fe^{3+}(salen)-POM gave the highest activity. Its activity is much higher than the Fe^{3+}(salen)Cl. The conversion for all substrates is >50% with >90% selectivity of ketone.

2.7.2 Heterogeneous catalysis

In 1999 Alexander M. *et al.* [20] studied the impregnation of $H_5PV_2Mo_{10}O_{40}$ onto MCM-41 and amino-modified MCM-41 materials. They were used for aerobic hydrocarbon oxidation using isobutyraldehyde as a reducing agent. The oxidation of alkenes and alkanes gave product selectivities similar to those observed in the corresponding homogeneous reaction although catalytic activity was lower. Under appropriate experimental conditions there was no leaching and the solid catalyst could be reused.

In 1999, Carvalho, et. al. [21] synthesized and characterized $M(NC_3)Si$-MCM-41(M = Cu(II) and Fe(III)) and M-MCM-41 catalysts. These catalysts were employed in the oxidation reaction of cyclohexane with aqueous H_2O_2 (reaction temperature 100°C, 12 h. They found that $M(NC_3)Si$-MCM-41 were more active than M-MCM-41. The activity of catalysts decreased in the following order: $Fe(NC_3)Si$-MCM-41 > Fe-MCM-41 > $Cu(NC_3)Si$-MCM-41 > Cu-MCM-41. However, when the catalysts were recycled, leaching of the metal was observed.

In 2004 S.E. Dapurkar *et al.* [22] studied oxidation of cyclohexane over mesoporous VMCM-41 molecular sieve catalyst using aqueous hydrogen peroxide as oxidant, acetic acid as solvent, and methyl ethyl ketone as initiator. The activity of catalyst slightly decreased after first recycle (from 99 to 93 %conversion), owing to leaching of small amount of non-framework vanadium ion. At the optimized condition cyclohexanol was obtained as the major product with 94.5% selectivity. The use of strong oxidizing agent, TBHP resulted in the formation of cyclohexanone as the major product 82.4% selectivity.

In 2006 Yuan *et al.* [23] studied oxidation of cyclohexane by molecular oxygen over metal-containing ZSM-5 catalysts in a solvent-free system. Among those M-ZSM-5 and M/ZSM-5 catalysts tested, Co-containing ZSM-5 catalysts including Co/ZSM-5 (prepared by ion-exchange and calcination) and Co-ZSM-5 (prepared by ion-exchange and drying) showed the best activity for the oxidation of cyclohexane to cyclohexanone and cyclohexanol. Co/ZSM-5 had almost the same activity as Co-ZSM-5 for the cyclohexane oxidation; however, the leaching of cobalt from Co-ZSM-5 readily occurred. Co/ZSM-5 (calcined) catalyst could achieve about 10 mol% conversion of cyclohexane and 97% selectivity of KA-oil (the mixture of cyclohexanone and cyclohexanol) at 393 K under the pressure of 1.0 MPa O_2.

In 2007 Dharmesh *et al.* [24] studied on the immobilization of the polyoxometalate $[PV_2Mo_{10}O_{40}]^{5-}$ on modified mesoporous MCM-41. The MCM-41 host material was made by functionalization of the surface with $[(MeO)_3\text{-}Si(CH_2)_3N^+(CH_3)_3]Cl$. POM is deprotonated and could be easily immobilized by wet impregnation of the modified silica using CH_3OH as the solvent. These techniques indicated that the POM is intact on the surface after impregnation. High loadings of POM caused a decrease in the surface area and pore volume of solid, presumably due to both pore blockage and restructuring of the silica during wet impregnation.

In 2008 Shahram *et al.* [25] synthesized vanadium polyoxometalate (PVMo) supported on MCM-41 and MCM-41-NH_2 for hydrocarbon oxidation with hydrogen peroxide. PVMo-MCM was prepared by introduction of PVMo into the mesoporous molecule sieves of MCM-41 by impregnation and adsorption techniques. Oxidation of the alkenes and alkanes gave product selectivities, similar to those observed for corresponding homogeneous catalyst. Ultrasonic irradiation has a particular effect on MCM-41 structural uniformity and reduced the reaction times and improved the product yields. In addition, the solid catalysts could be recovered and reused several times without loss of activity.

In 2008 Jiquan *et al.* [26] synthesized secondary amino group modified MCM-41 and used as a support for the immobilization of a salen oxovanadium complex via a multi-grafting method. The immobilized complex was an effective catalyst for oxidation of cyclohexane using H_2O_2 under mild conditions. A conversion of 45% of cyclohexane was obtained with a selectivity of 100% of the cyclohexanone/cyclohexanol mixture when the reaction was run at 60 °C for 12 h in acetonitrile.

In 2009 Sreevardhan *et al.* [27] synthesized Co-SBA-15 catalysts by direct synthesis and post-synthetic impregnation methods at two different loadings of Co viz., 1.2 and 2 wt%. The structure of SBA-15 was found to remain intact even after the incorporation of Co. The encapsulation of Co in SBA-15 was found to be highly advantageous in yielding significant amounts of the desired products (cyclohexanone and cyclohexanol) in the oxidation of cyclohexane without using any solvent under moderate pressure of O_2 at 433 K. 2 wt% Co-SBA-15 catalyst showed 9.4% conversion of cyclohexane and 78% selectivity of cyclohexanone.