

CHAPTER I

INTRODUCTION

There are many competitions in chemical industries. Expansions in industries induce the needs for developing new methodology. Among general chemicals required, alcohols are manifestly such important starting materials in chemical industries. Because of their versatile functional group and their availability in large amounts at low prices, there are many approaches to obtain alcohols from organic raw materials, petroleum, natural gas, coal and biomass.¹ A selected example is illustrated in Fig 1.1.

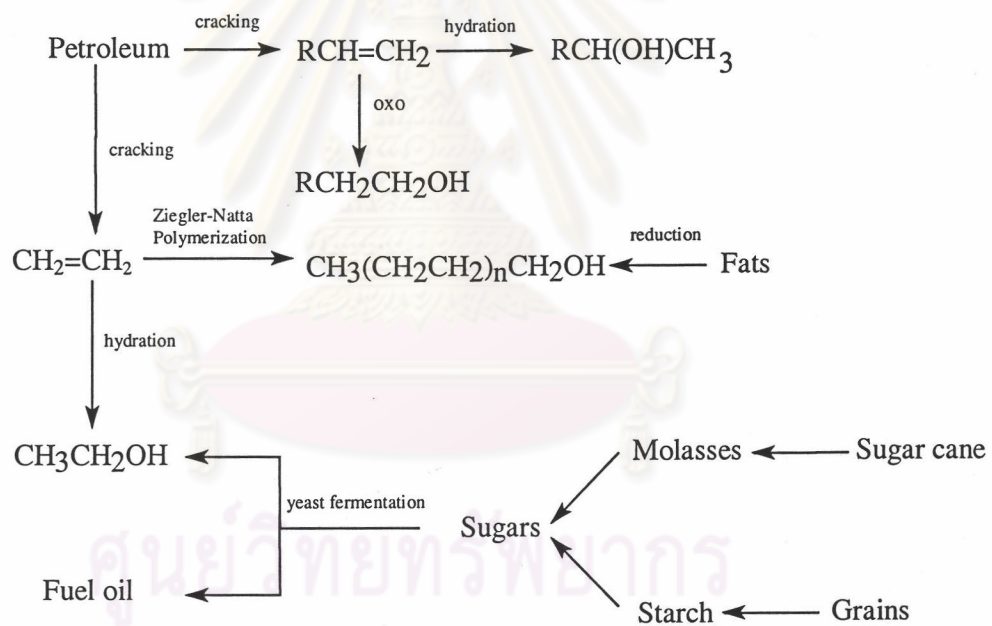


Fig 1.1 Industrial sources of alcohol

Important alcohols used in industrial processes are methyl alcohol and ethyl alcohol. Prior to the development of the modern chemical industry, methyl alcohol is highly poisonous; the result was an alarming number of deaths and cause of blindness. Methanol was used for the manufacture, jet fuels, radiator antifreeze and solvent and for denaturing ethyl alcohol. For ethyl alcohol, one of industrial alcohols used for

non-beverage purpose and currently intermediates in other industrial processes. Hydrolysis of ethylene in sulfuric acid give ethanol.



Reaction of alcohols can be divided into two groups: that one reaction occurs at the C-O bond and the other occurs at the O-H bond.

One of the most important reactions of alcohol is oxidation to yield carbonyl compounds. Primary alcohols yield aldehydes or carboxylic acids, secondary alcohols yield ketones and tertiary alcohols do not react with most oxidizing agents except under the most vigorous conditions. Oxidation reaction of alcohols can convert in a variety of products such as carboxylic acid, ester, α -hydroxy hydroperoxide and *etc.* Oxidation of primary alcohols to carboxylic acids is not a difficult task. The product can occur at higher temperature or at longer reaction times. The reaction has been accomplished with nitric acid or sometimes potassium hydroxide was used as oxidant. Oxidation of primary alcohols to esters reacted in acidic media. The important features that make the reaction occur are substrate, oxidant or oxidizing agent, solvent system and catalyst.

The discovery of oxidants that are able to achieve the conversion of alcohol to carbonyl compound in high yield has been of key importance to the development of the synthesis of complex natural products. Various oxidants are employed depending on reaction conditions, viability in conversion to product. Oxidants can be divided into many types. For example,

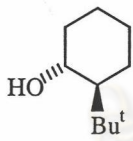
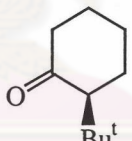
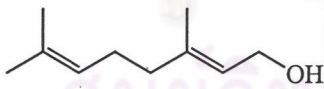
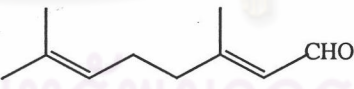
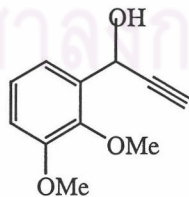
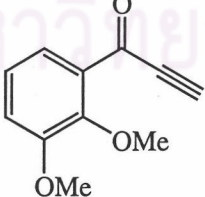
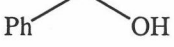
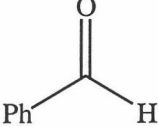
1. Alkaline potassium permanganate solution ($\text{KMnO}_4 + \text{OH}^-$)
2. Hot, concentrated HNO_3
3. Chromic acid: H_2CrO_4 prepared *in situ* from CrO_3 with aqueous H_2SO_4 (Jones' reagent) or $\text{Na}_2\text{Cr}_2\text{O}_7$ with aqueous H_2SO_4 .
4. Chromium trioxide (CrO_3) complexes with pyridine or with pyridine and HCl .

In addition, other oxidants that widely used in oxidation reaction and gave high efficiency are molecular oxygen, hydrogen peroxide (H_2O_2) and *tert*-butylhydroperoxide (TBHP).

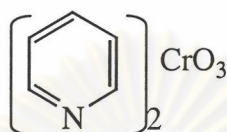
1.1 Classical methodologies for alcohol oxidation

Many researches are focused on oxidation, especially the search for versatile and selective reagents. Air, the cheapest oxidant, is the important oxygen source. Examples of oxidation by air alone are the conversion of aldehydes into carboxylic acids (autoxidation) and the oxidation of acyloins to α -diketones.² Chromium reagents are probably the most powerful and widely used of all oxidizing agents but over oxidation will occur for utilizing this reagent. Chromium(VI) in aqueous sulfuric acid is very strong oxidant using to oxidize primary alcohol. The uses of acetic acid increased the solubility of organic substance and also increased the rate of oxidation *via* acid catalysis. Interestingly, chromium in aqueous sulfuric acid/acetone (Jones' oxidation), one of the best known and most widely used methods of oxidation using chromium(VI). Some oxidation reactions using chromium(VI) as oxidant is shown in Table 1.1.

Table 1.1 Oxidation of alcohol in aqueous sulfuric acid/acetone (Jones oxidation)³

Entry	Substrate	Product	Yield (%)
1			40
2			91
3			71
4			76

Collins reagent was derived from the reaction of chromium(VI)oxide with two molecules of pyridine. This reagent could transform alcohols to their analog carbonyl compounds in moderate to excellent yield. It is not acedic acid, consequently, is very suitable for oxidation of acid-sensitive substrate. Corey and coworkers developed pyridinium chlorochromate (PCC) in 1977.⁴ The obtained products are ketone and aldehyde. The data shown above was clearly seen that chromium could utilize in many forms.

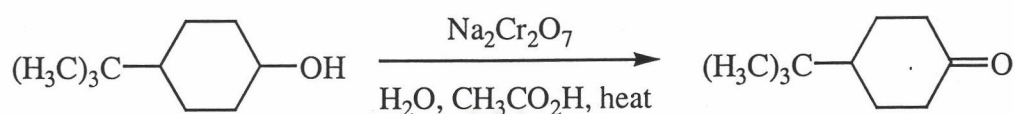


Some selected examples using $\text{CrO}_3 \cdot \text{py}_2$ (Collins oxidation) are shown in Table 1.2.

Table 1.2 Oxidation of alcohols with $\text{CrO}_3 \cdot \text{py}_2$ (Collins oxidation)⁵

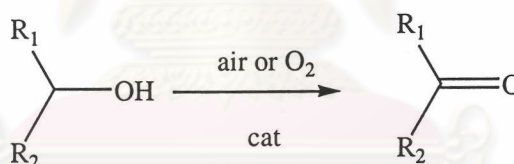
Entry	Substrate	Product	Yield (%)
1			73
2			89
3			71
4			92

Another pyridine-chromium trioxide complex, pyridinium chlorochromate, $C_5H_5NHCrO_3Cl$ (PCC), which is commercially available, has been widely used as oxidizing agent. In addition, secondary alcohols are oxidized easily in high yields to give ketones. For large-scale oxidations, an inexpensive reagent such as sodium dichromate in aqueous acetic acid was frequently used.



1.2 Literature review of metal catalysed oxidation reaction

The catalytic oxidation of alcohol over metal, metal oxide and salts is an industrially important process. In laboratory, catalytic oxidation of alcohol is most often performed in aqueous or organic solution, with oxygen over platinum catalyst. Under atmospheric system, the air oxidation is the simple method, safe, clean and available free. Observation in 1998 by I. E. Marko and colleagues found that utilizing dioxygen (or air) as a stoichiometric oxidant in alcohol oxidation gave carbonyl derivatives in high yield.⁶



The catalysts employed are $CuCl$ /phenanthroline, tetrapropylammonium perruthenate (TPAP).

In 1998, R. C. Larock and K. P. Peterson investigated an efficient procedure for the oxidation of primary and secondary allylic and benzylic alcohols. This has been achieved using catalytic $Pd(OAc)_2$ similar to the methodology employed by S. Uemura, but dimethylsulfoxide (DMSO) coupled with oxygen gas were used as an oxidant.⁷ The results showed that the reaction rates were increased and the yields with the addition of 2 equiv of $NaHCO_3$ were improved.

Employing of dioxo complex of ruthenium(VI), T. J. Mayer and Estelle L. Lebeau observed in 1999 that benzyl alcohol could be oxidized to yield benzaldehyde in water and acetonitrile.⁸ In the same year, J. Wiley found that the oxidation of allylic alcohol by alkaline species of periodate, $H_2IO_6^{3-}$, was catalysed by micro amount of $Pd(II)$ in 0.2 mol/dm^3 alkaline solution.⁹ The active species of the catalyst

was found to be PdCl^+ . Other metals that used in oxidation such as ruthenium complex of N,N',N'' -trimethyl-1,4,7-triazacyclononane were used as catalyst in chemoselective oxidation of benzyl alcohol to benzaldehyde (98% yield) using TBHP as terminal oxidant reported by Chi-Ming Che.¹⁰ In 1999, S. Uemura and his colleagues disclosed the use of molecular oxygen as an oxidant in the oxidation reaction carried out in the presence of $\text{Pd}(\text{OAc})_2/\text{pyridine}/\text{MS3A}$.¹¹ After that in 2001, they developed Pd(II) acetate-pyridine complex supported by hydrotalcite in toluene oxidized by air system.¹² This catalyst system could oxidize a variety of primary and secondary alcohols into the corresponding aldehydes and ketones in high yield. The catalyst can be easily prepared from all commercially available reagents and could be reused several times.

In 2000, P. A. Shapley reported the selective alcohol oxidation with molecular oxygen catalysed by Os-Cr and Ru-Cr complexes.¹³ In 1999, the report concerning about the improvement of alcohol oxidation using aqueous permanganate and phase-transfer catalyst was addressed. L. Powell and co-worker found that 4,4,5,5,5-pentafluoropentanol (PFP) could be oxidized to pentafluoropentanoic acid (PFPeA) in 77% yield using sodium permanganate in the presence of tetraethylammonium hydrogen sulphate.¹⁴ Sometimes the strong oxidant might cause of over oxidation like the utilization of permanganate in previous mentioned reactions.

It was notified that almost oxidation reaction using metal or metal complex as a catalyst increased reaction rate. Metals that used in industries as catalyst were chromium, cobalt, iron, copper, palladium, manganese and platinum, *etc.* Catalysts become an important factor in reaction. Heterogeneous and homogeneous catalysts are both used in industries.

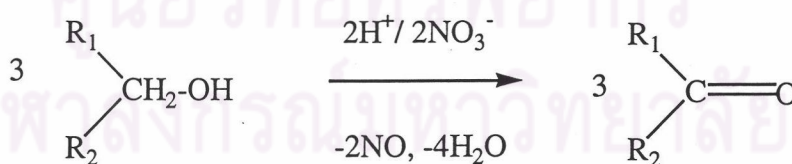
1.3 Literature review on iron-catalysed oxidation reactions of alcohols

An example involving the alcohol oxidation catalysed by iron complexes was reported by A. Nakamura and co-workers in 1993. They accomplished to oxidize benzoin to benzil and of *p*-substituted benzyl alcohol to the corresponding benzaldehyde catalysed by iron(II)thiolate complex under mild conditions (in DMF at 25°C and ambient pressure).¹⁵ The Fe(II)thiolate complex exhibited high catalytic activity with fast oxidation reaction.

In 1994, D.H.R. Barton disclosed the modified Gif-type system using *tert*-butylhydroperoxide (TBHP) as an oxidant for alcohol oxidation.¹⁶ Fe(III) species was used as a catalyst. The results showed that the efficiency of the reaction based on one mole of product derived from one mole of oxidant gave a quantitative efficiency of TBHP for this system.

Iron salts and iron complexes were reported to utilize as a catalyst in oxidation of alcohol. Iron can be used in many forms like Fe(II), Fe(III) and other forms. Ferrate (FeO_4^{2-}) has been recently investigated by K. Yoshizawa in 2001.¹⁷ Ferrate was used in oxidation of methanol to formaldehyde. Ferrate derived from mineral salts such as the potassium (K_2FeO_4) and barium (BaFeO_4) forms, could mediate the oxidation of a wide variety of organic compounds such as alcohols, amines, hydrazines, peroxides, hydrocarbons, and thiosulfates with excellent selectivity. They observed that in an acidic media, ferrate is protonated and its oxidation ability is greatly increased.

Catalysts on solid support become interesting and have been widely studied. Because of the property of supported catalysts provided the ease of set up, work up, use mild experimental condition and provide good yield and/or selectivity. During the last few years, A. Cornelis and P. Laszlo have developed supported catalyst to use in oxidation.¹⁸ The oxidation of alcohol to carbonyl compounds under mild conditions using supported reagent could be carried out fruitfully. The method based on the use of iron(III)nitrate impregnated on K-10 bentonite clay. The reaction was carried out with subsequent air oxidation of NO to NO_2 . Iron(III)nitrate supported on bentonite clay or copper(II)nitrate supported on bentonite clay could be successfully utilized as a catalyst in oxidation of benzyl alcohol in high yield (100%).



The method for preparing support bentonite clay is not complex. Dissolution of iron(III)nitrate nonahydrate in acetone, mud occurred and light brown suspension appeared after that bentonite clay was added. Finally the solvent was removed by evaporation.¹⁹ In 2001, Antony R. synthesized and examined the catalytic activity of Fe(III) on a polystyrene-Schiff base support.²⁰ These supported catalysts were found to be effective in the epoxidation of *cis*-cyclooctene and styrene in the presence of TBHP under mild conditions.

In this research, cyclohexanol, benzyl alcohol and 2-octanol, three model alcohols were employed. For cyclohexanol, the major product from the oxidation of cyclohexanol was cyclohexanone. A mixture of cyclohexanol and cyclohexanone are the starting material for making adipic acid and caprolactam. Adipic acid was the principal reactant for the production of nylon 66. Cyclohexanone is the starting reactant for caprolactam, a raw material for nylon 6.

For octanol, the total United State of America demand for octanols in 1965 was 295.0 million pounds. Most of them were employed as plasticizers. Plasticizers are used mainly in PVC compounding, the most important being the phthalates. Ester of aliphatic acids is used in applications where low-temperature flexibility is required, *e.g*; footwear and household refrigerator parts. Epoxidized plasticizers are made by esterification of oleic acid, followed by epoxidation. Miscellaneous uses are mainly in the lube-oil additive field.

1.4 The goal of this research

The purpose of this research can be summarized as follows;

1. To synthesize iron complexes from Schiff base ligands and 1,3-dicarbonyl ligands.
2. To study the optimum conditions for oxidation of model alcohols using iron complexes.
3. To comparatively explore the alcohol oxidation using iron complexes and iron catalysts on support.

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