Catalytic Oxidation

Principles and Applications

edited by

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CATALYTIC OXIDATION: PRINCIPLES AND APPLICATIONS

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Preface

Selective catalytic oxidation is a key technology for converting oil and natural gas-derived feedstocks to a wide variety of bulk chemicals. Moreover, in the wake of increasingly stringent environmental legislation, attention is being focused on the development of 'greener' processes, such as catalytic oxidation, for the manufacture of fine chemicals. A thorough understanding of fundamental mechanistic pathways of catalytic oxidations is of paramount importance for the improvement of existing processes and the development of new ones. Hence, the substantial interest, in both industrial and academic laboratories, in the mechanisms of oxidation catalysis.

Compared to hydrogenations, for example, which are mechanistically relatively straightforward processes, oxidations are enormously complex. For starters, molecular oxygen, in contrast to hydrogen, reacts with most organic molecules even in the absence of a catalyst. Hence, a thorough knowledge of these free radical chain processes (autoxidations) is an essential ingredient for understanding oxidation catalysis.

Catalytic oxidations with molecular oxygen (dioxygen) can be divided into two types: heterogeneous, gas phase and homogeneous, liquid phase processes. Researchers generally affiliate themselves with one or the other group and the two tribes speak largely different languages. Consequently, there is little cross-fertilization of ideas and, moreover, a third type-heterogeneous catalysis in the liquid phase- tends to suffer from lack of attention by either group.

A major aim of this book is to provide a sound mechanistic basis for understanding catalytic oxidation processes, which should be useful to reseachers in the field, irrespective of their tribal affiliation. It is based on a course on oxidation catalysis held in Rolduc, The Netherlands, in June 1994, under the auspices of the Dutch Research School in Catalysis (NIOK). The course was given by international authorities from industry and academia in the fields of both gas and liquid phase oxidations. It was targeted mainly at postgraduate research students wanting to acquaint themselves with the basic principles and industrial applications of oxidation catalysis. Moreover, it was hoped that the course would foster a synergistic cross-fertilization of concepts and ideas between the aforementioned groups. The participants had backgrounds ranging from surface science to organic synthesis.

The opening chapter (Sheldon) consists of an introductory overview of the subject, in which different processes to particular products are compared and the reader is introduced to mechanistic aspects. This is followed by a chapter (Haber) dealing with the elementary mechanisms of hydrocarbon oxidations on metal oxide surfaces and emphasizing the role of electrophilic versus nucleophilic oxygen species. Chapter three (Vedrine) contains a further description of the general features of oxidations on metal oxides, including multicomponent systems. The role of Mars -van Krevelen type mechanisms is emphasized. Chapter four (van Santen) continues with a detailed description of the mechanistic features of two industriallly important gas phase processes: the oxidation of ethylene to ethylene oxide and vinyl acetate, over silver and palladium-based catalysts, respectively. The elementary reaction steps taking place on the metal surface form the basis for this discussion,

Chapter five (Schmidt and Huff) focuses on the high-temperature oxidation of small molecules on noble metal catalysts. Four industrially important processes are discussed: ammonia oxidation to nitric acid, methane oxidation to syngas and ammoxidation to hydrogen cyanide, and oxidative dehydrogenation of ethane. A consideration of mass and heat transfer effects in conjunction with reaction kinetics is shown to be fundamental to understanding these processes. Chapter six (Marin), continuing in the same vein, elaborates the reaction pathways involved in the high-temperature oxidative coupling of methane. The consequences of the interplay between chemical kinetics and mass transfer for the selectivity to ethane and ethylene are highlighted. Chapter seven (van Veen) strikes a different note by discussing the principles and prospects of fuel cells, in which the basic reaction is equivalent to the combustion of hydrogen.

The second part of the book is devoted to liquid phase oxidation processes. It opens in chapter eight (Sheldon) with a review of the basic principles of free radical chain autoxidations. The intricate mechanism of the Amoco process for the catalytic oxidation of p-xylene to terephthalic acid is discussed in detail. Chapter nine (Sheldon) continues with an elaboration of the various types of heterogeneous catalysts for liquid phase oxidations. Particular emphasis is placed on molecular sieve catalysts containing redox metal ions incorporated in the framework or metal complexes encapsulated in the micropores (ship-in-the-bottle catalysts).

Chapter ten (Moiseev) elucidates the mechanistic roles of σ and π complexes in palladium-catalyzed oxidations of olefins. The oxidative acetoxylation of ethylene and propylene, to vinyl acetate and allyl acetate, respectively, catalyzed by giant palladium clusters is discussed. The latter can be considered as bridging the gap between homogeneous palladium complexes and a palladium metal surface. Chapter eleven (Sheldon) is devoted to the application of catalytic oxidations in fine chemicals synthesis. The characte-

ristics of fine versus bulk chemical manufacture and catalytic oxidation versus oxygen transfer are explained. It also includes a section on catalytic asymmetric oxidation. This part of the book concludes with a chapter (van Veen) on selective electrochemical oxidations, encompassing both ex-situ and in-situ generation of metal oxidants. Attention is also focused an new developments in electrode materials and solid polymer electrolyte cells.

The third part of the book, chapter thirteen (Mills, Harold and Lerou), returns to the subject of heterogeneous gas-phase processes with a comprehensive overview of catalytic reactor technology. The advantages and limitations of existing and emerging catalytic reactors are discussed.

The book contains more than 600 literature references and a thoroughy cross-referenced index. Hopefully it will be widely used by aspiring researchers in this fascinating and economically important field. Finally, the editors would like to express their sincere thanks to their friends and colleagues who have contributed chapters to this book and Frank Sheldon for preparing the index.

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CATALYTIC OXIDATIONS: AN OVERVIEW

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ABSTRACT

Processes for the manufacture of industrial chemicals by catalytic oxidation of feedstocks derived from oil or natural gas are reviewed. Both heterogeneous, gas phase and homogeneous liquid phase processes are discussed and different processes to particular products, such as acetic acid, propylene oxide, phenol and cyclohexane, are compared. Recent trends in chemicals manufacture are also outlined. Finally, the reader is introduced to mechanistic aspects of metal oxidations.

1. Introduction

The controlled partial oxidation of hydrocarbons, comprising alkanes, alkenes and aromatics, is the single most important technology for the conversion of oil- and natural gas-based feedstocks to industrial organic chemicals[1-3]. For economic reasons, these processes predominantly involve the use of molecular oxygen (dioxygen) as the primary oxidant. Their success depends largely on the use of metal catalysts to promote both the rate of reaction and the selectivity to partial oxidation products. Both gas phase and liquid phase oxidations, employing heterogeneous and homogeneous catalysts, respectively, are practiced industrially. (Table 1).
Moreover, the pressure of increasingly stringent environmental regulation is stimulating the deployment of catalytic oxidation in the manufacture of fine chemicals (see chapter 11). Traditionally, the production of many fine chemicals has involved oxidations with stoichiometric quantities of, for example, permanganate or dichromate, leading to the concomitant generation of large amounts of inorganic salt - containing effluent. Currently there is considerable pressure, therefore, to replace these antiquated technologies by cleaner, catalytic alternatives[4-8].

2. Homogeneous Catalysis / Liquid phase

Several important liquid phase processes were developed during the 1950's and 1960's. Examples include the Wacker process for ethylene oxidation to acetaldehyde, the Celanese process for n-butane oxidation to acetic acid and the Amoco/Mid-Century process for the production of terephthalic acid from p-xylene (figure 1).
Although, as noted above, catalytic oxidation is the most favorable technology for the manufacture of many industrial chemicals this is not always the case. The most important process for the production of acetic acid, for example, is the rhodium-catalyzed carbonylation of methanol developed by Monsanto[9] (see figure 2). This process has the advantage of high selectivity (99%) coupled with cheap raw materials (methanol and carbon monoxide).

Table 1. Catalytic Oxidation Processes.

Product	Primary raw materials	Volume [a] (10^6 tons)	Oxidant/ Process
Styrene	Benzene / ethylene	5.0	None/G
Terephthalic acid	p-Xylene	3.9	O_2 /L
Formaldehyde	Methanol	3.8	O_2 /G
Ethylene oxide	Ethylene	2.9	O_2 /G
Phenol	a. Benzene / propylene b. Toluene	1.9	O_2 /L
Acetic acid	a. n-Butane b. Ethylene	1.8	O_2 /L
Propylene oxide	Propylene	1.4	RO_2H /L
Acrylonitrile	Propylene	1.4	O_2 /G
Vinyl acetate	Ethylene	1.3	O_2 /L;G
Acetone	Propylene	1.2	O_2 /L
Benzoic acid	Toluene	1.0	O_2 /L
Adipic acid	Benzene	0.9	O_2 /L
Caprolactam	Benzene	0.7	O_2 /L
Phthalic anhydride	o-Xylene	0.7	O_2 /G
Methyl methacrylate	Isobutene	0.5	O_2 /G
Acrylic acid	Propylene	0.5	O_2 /G
Methyl ethyl ketone	1-Butene	0.3	O_2 /L
Maleic anhydride	n-Butane	0.3	O_2 /G

a. USA, 1993 b. L=liquid phase; G=gas phase c. Acetic acid predominantly made via methanol carbonylation

3. Heterogeneous Catalysis / Gas Phase

Several important gas phase oxidation processes are outlined in figure 3. These processes were developed in the 1950's or earlier, although process improvements are still being made, e.g. in maleic anhydride manufacture from n-butane (see chapter 12).

The manufacture of methylmethacrylate (MMA) is an interesting case in point for comparing different technologies (see figure 4). The classical process involves the methanolysis of acetone cyanohydrin, has an atom utilization[5-8] of 29%, and produces 2.5 kg. of ammonium bisulfate per kg of MMA. More recently Asahi and Mitsubishi have developed alternative processes[10] based on the gas phase, catalytic oxidation of isobutene to methacrolein analogous to the oxidation of propylene to acrolein (see figure 3). Alternatively, methacrylic acid can also be prepared in a two-step, oxidation/dehydrogenation of isobutyraldehyde. The latter is a byproduct of propylene hydroformylation to n-butyraldehyde. Routes have also been developed based on ethylene carbonylation or hydroformylation[10] (see figure 4). Finally, Shell workers [11] have reported an elegant one-step synthesis of MMA by methoxycarbonylation of methylacetylene, the latter being available as a byproduct of naphtha cracking.
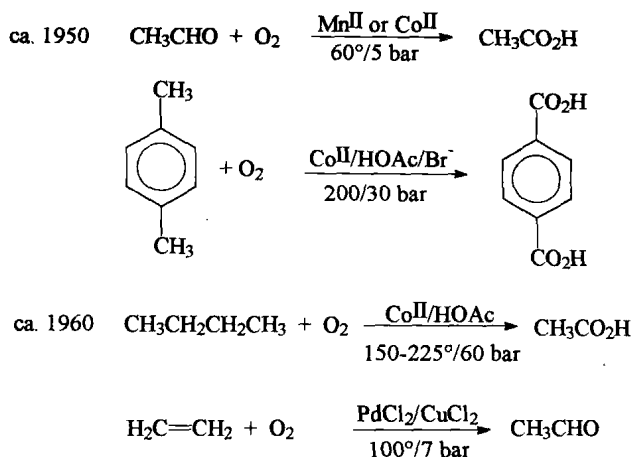
ca. 1950 $CH_3CHO + O_2$ $\xrightarrow[60°/5 \text{ bar}]{Mn^{II} \text{ or } Co^{II}}$ CH_3CO_2H

$$\underset{\overset{\displaystyle |}{CH_3}}{\overset{\overset{\displaystyle CH_3}{|}}{\bigcirc}} + O_2 \xrightarrow[200/30 \text{ bar}]{Co^{II}/HOAc/Br^-} \underset{\overset{\displaystyle |}{CO_2H}}{\overset{\overset{\displaystyle CO_2H}{|}}{\bigcirc}}$$

ca. 1960 $CH_3CH_2CH_2CH_3 + O_2$ $\xrightarrow[150-225°/60 \text{ bar}]{Co^{II}/HOAc}$ CH_3CO_2H

$H_2C{=}CH_2 + O_2$ $\xrightarrow[100°/7 \text{ bar}]{PdCl_2/CuCl_2}$ CH_3CHO

Figure 1. Liquid phase Oxidation Processes.

4. Propylene Oxide Manufacture: the Selectivity Problem

Table 1 contains one example of an industrial process, the manufacture of propylene oxide, that is notable in two respects : it involves the use of an alkyl hydroperoxide as the primary oxidant and, in one variant of the process at least, a heterogeneous catalyst in the liquid phase. As noted above, (figure 3) ethylene oxide is produced by gas phase oxidation of ethylene over a silver catalyst. Unfortunately, oxidation of propylene under the same conditions is unselective, due to competing oxidation of the olefinic double bond and the allylic C-H bonds.
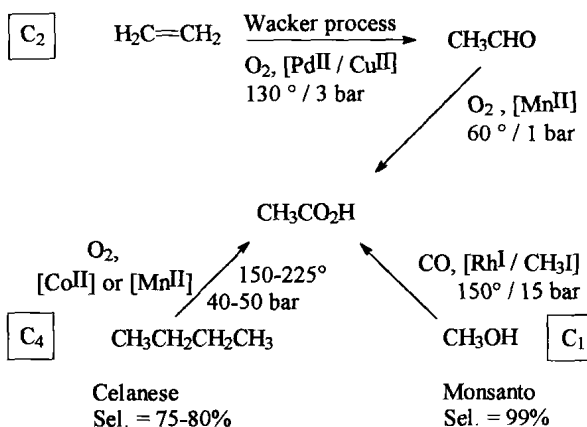
$\boxed{C_2}$ $H_2C{=}CH_2$ $\xrightarrow[\substack{O_2, [Pd^{II}/Cu^{II}] \\ 130°/3 \text{ bar}}]{\text{Wacker process}}$ CH_3CHO

$O_2, [Mn^{II}]$
$60°/1 \text{ bar}$

CH_3CO_2H

$O_2,$
$[Co^{II}] \text{ or } [Mn^{II}]$ $150-225°$
$40-50 \text{ bar}$

$CO, [Rh^I/CH_3I]$
$150°/15 \text{ bar}$

$\boxed{C_4}$ $CH_3CH_2CH_2CH_3$ CH_3OH $\boxed{C_1}$

Celanese
Sel. = 75-80%

Monsanto
Sel. = 99%

Figure 2. Acetic Acid Manufacturing Processes.

$$H_2C=CH_2 + 1/2\ O_2 \xrightarrow[250°C]{[Ag/Al_2O_3]} H_2C-CH_2\ (O)$$

Shell / Union Carbide, 1935

$$CH_3CH=CH_2 \xrightarrow[400°C]{[Bi_2MoO_6]}$$

$$\xrightarrow{O_2} H_2C=CHCHO$$

$$\xrightarrow[NH_3]{O_2} H_2C=CHCN$$

Sohio, 1959

ortho-xylene (CH_3, CH_3) $\xrightarrow[O_2\ ;\ 350°C]{[V_2O_5/TiO_2]}$ phthalic anhydride

$$CH_3CH_2CH_2CH_3 \xrightarrow{V_2O_5\ /\ P_2O_5} \text{maleic anhydride}$$

Monsanto, Lonza, Dupont
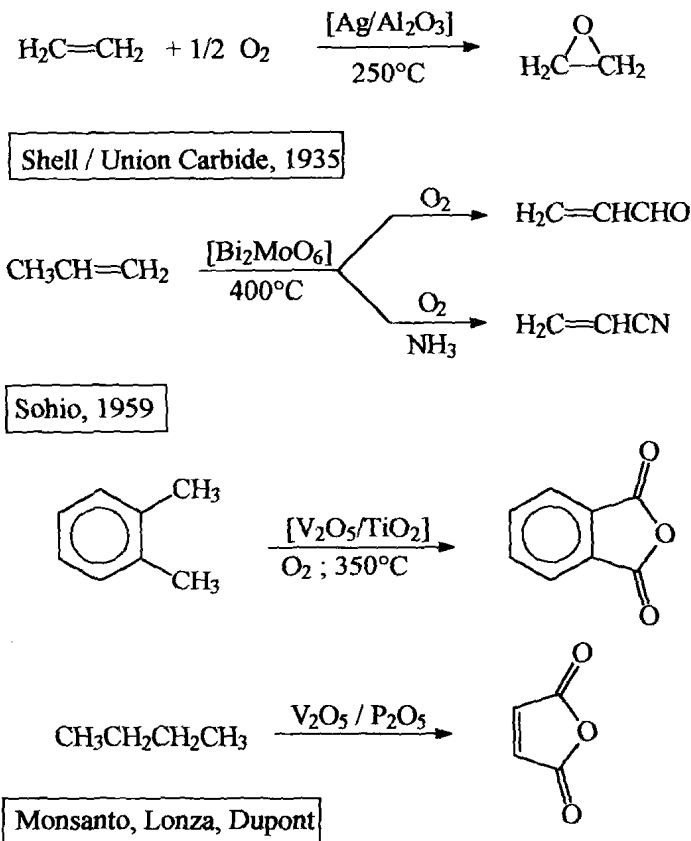
Figure 3. Gas Phase Oxidation Processes

Propylene oxide was traditionally produced via the chlorohydrin process. However, this low atom utilization process produces about 2 kg of $CaCl_2$ per kg of propylene oxide. The Arco process[3,12], in contrast, utilizes an alkyl hydroperoxide, e.g. tert-butyl hydroperoxide, in the presence of a homogeneous molybdenum catalyst. The tert-butanol coproduct is converted to the gasoline extender, methyl tert-butyl ether (MTBE). The overall process constitutes the conversion of the basic raw materials, propylene, isobutane, methanol and oxygen, to propylene oxide and MTBE together with a molecule of water. In the Shell SMPO process (styrene monomer propylene oxide) ethylbenzene hydroperoxide is used in conjunction with a heterogeneous titanium(IV)/silica catalyst[3,12]. In this case the alcohol coproduct is dehydrated to styrene, giving an overall transformation of ethylbenzene, propylene and oxygen to styrene, propylene oxide and water.
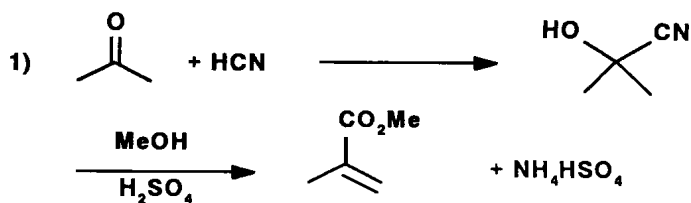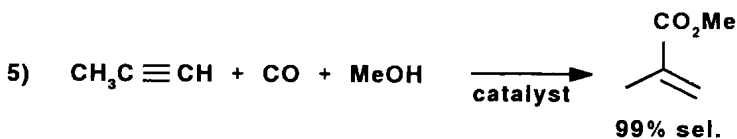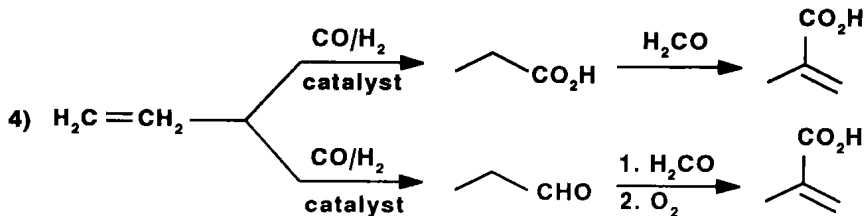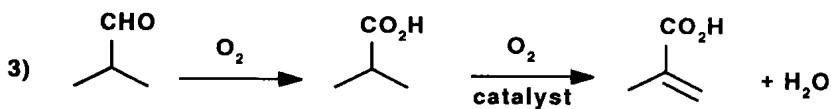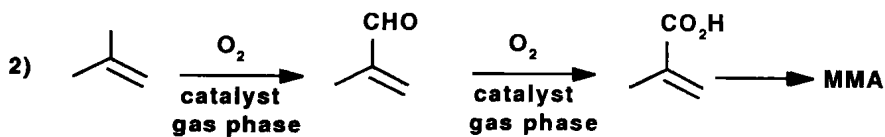
Figure 4. Alternative Routes to Methylmethacrylate.

CHLOROHYDRIN PROCESS

ca. 2 kg $CaCl_2$ per kg PO
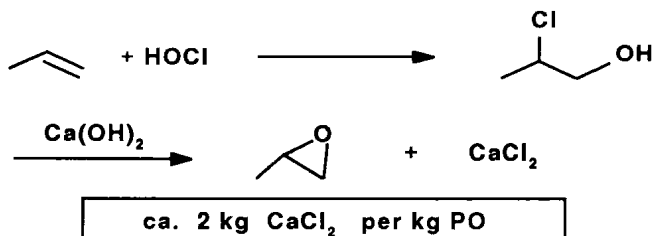
CATALYTIC EPOXIDATION
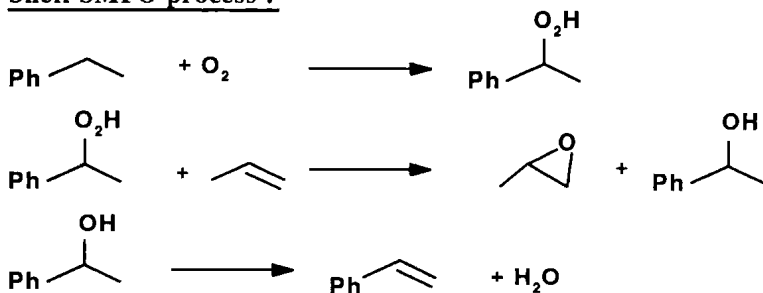### Arco process :
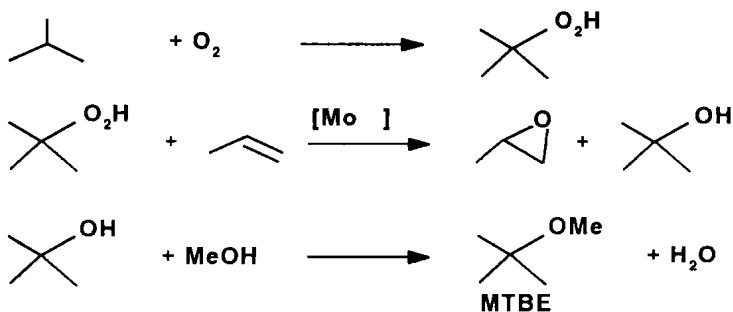

Shell SMPO process :

Figure 5. Routes to propylene oxide.

5. Manufacture of Aromatic Acids

As noted above, phthalic acid (anhydride) is produced by gas phase oxidation of o-xylene over a vanadium oxide catalyst. In contrast most other aromatic carboxylic acids are produced by metal-catalyzed autoxidation of the corresponding toluene in the liquid phase (reaction 1).

$$ArCH_3 + 1\frac{1}{2}O_2 \xrightarrow{\text{Catalyst}} ArCO_2H + H_2O \qquad (1)$$
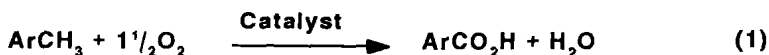
Traditionally many aromatic carboxylic were produced by nitric acid oxidation of the corresponding toluene or by side chain chlorination followed by hydrolysis. Unfortunately, these processes suffer from serious drawbacks: large amounts of inorganic salt-containing effluent and chloro(nitro) compounds as impurities. Catalytic oxidation, on the other hand, is a high atom utilization, low salt process with no chloro(nitro) compounds as impurities.

Benzoic acid, for example, is produced commercially by the cobalt-catalyzed autoxidation of toluene (see chapter 8). The most important aromatic carboxylic acid is, however, terephthalic acid (see Table 1). It is produced by autoxidation of p-xylene in acetic acid in the presence of a cobalt catalyst and a promotor : either acetaldehyde (Eastman-Kodak and Toray processes) or bromide ion (Amoco/MC process)[13]. The two processes are compared in Table 2. The mechanism of the bromide ion promoted catalysis is discussed in chapter 9.

Table 2. Terephthalic Acid Manufacture.

	Cooxidation (Eastman Kodak/ Toray)	Bromide-mediated (Amoco-MC)
Catalyst	$Co(OAc)_2$	$Co(OAc)_2/ Mn(OAc)_2$
Solvent	HOAc	HOAc
Promotor	CH_3CHO	Br^-
Temp. (°C)	100-140	195
Pressure (bar)	30	20
Conv./ Sel. (%)	>95/ >95	>95/ >95
Advantage	Less corrosion	Lower [catalyst]
Disadvantage	Coproduct HOAc (0.21 $^t/_t$)	Corrosive (Ti-lined reactor)

6. Phenol Manufacture: Benzene versus Toluene as primary building block

The two industrial routes to phenol are outlined in figure 6. The benzene-based cumene process is more selective but this tends to be offset by the lower price of toluene and the lower number of steps (two compared to three). Direct hydroxylation of benzene remains a potentially attractive alternative but up till now yields and/or productivities are much too low to be competitive.
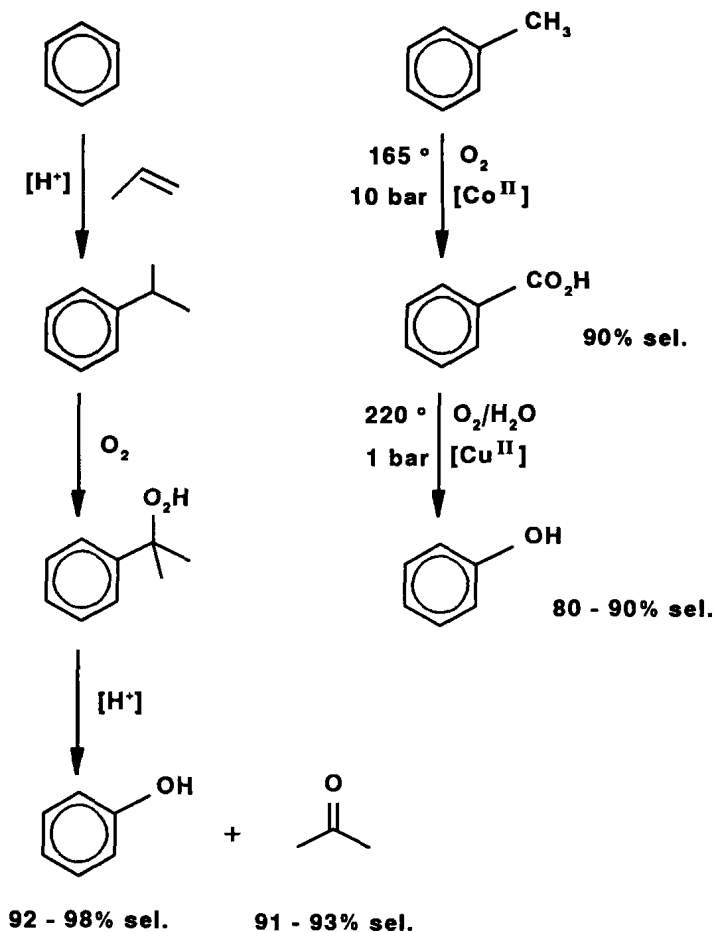
Figure 6. Two Routes to Phenol.

7. Caprolactam Manufacture: the Salt Issue

Caprolactam is an excellent example to illustrate the role of catalytic oxidations and reductions in chemicals manufacture. A key intermediate in most processes is cyclohexanone which is produced by the autoxidation of cyclohexane or hydrogenation of phenol (figure 7).