

HANDBOOK OF  

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COMMERCIAL  
CATALYSTS  

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HETEROGENEOUS  
CATALYSTS

HOWARD F. RASE

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HOWARD F. RASE

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# Preface

This handbook is written for chemical engineers and chemists who are involved in selecting or improving an existing process. It has been my goal to supply information based on the open literature that you can use to quickly gain background on a particular process or catalyst. For each reaction that is presented, the following topics are discussed.

- Product uses
- Chemistry
- Mechanism
- Catalyst type
- Catalyst suppliers and licensors
- Catalyst deactivation
- Catalyst regeneration
- Process units (description)
- Process kinetics

With such information, you can be prepared to begin rational analysis of an existing or planned reaction system and logically discuss catalyst characteristics and operations with technical representatives of catalyst manufacturers as well as your own colleagues.

The original definition of a handbook, *a conveniently carried and concise reference book*, has only partially survived as more important and valuable information becomes available. I have, however, been determined to make this handbook concise and easy to use as a means for quickly finding information on 150 major industrial processes using heterogeneous catalysts. This goal has been accomplished by using the same outline for each process, by including hundreds of tables and figures that serve to consolidate important concepts, by listing catalyst suppliers and licensors for each process, by using a single writing style and organization made possible by being the sole author, and by providing copious references for further study.

Despite the major developments in understanding, many of the phenomena that occur on a catalytic surface, and much of successful catalyst development and use, continues to be part science and part art. In fact, detailed understanding of a new catalyst often follows its initial invention. Hence, another goal for this handbook has been to facilitate the effective combination of significant studies by the research and development community with practical knowledge or art. Much of the latter is proprietary for each process, but valuable general insights have been published and included in this book when considered appropriate and useful. Excellent literature, including use recommendations, is also available from catalyst suppliers.

In contrast to the study of semiconductors used in the electronics industry, where the model system for laboratory study is the same as the real system, most catalysts are polycrystalline and not amenable to many advanced surface-science techniques which require single crystals (catalytic converter catalyst used in auto exhaust systems is an exception). Studies on single crystals, however, when combined with other insights, can yield valuable postulates about the mechanism of commercial catalysts. As always, there are various possible interpretations. But a postulated mechanism or reaction scheme based on rational concepts, even not totally verified, can provide a framework for developing useful explanations for observed catalyst behavior in industrial reactors and lead to improved operation and/or even improved catalyst formulations.

Finally, in addition to practical experience within one's own organization, technical representatives of catalyst suppliers and licensors are valuable fountains of knowledge on catalysts produced

by their companies. Their help in catalyst selection as well as catalyst development should be sought in the early stages of a project as well as in ongoing efforts directed at process improvement.

**Howard F. Rase**  
**Austin, Texas**

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# About the Author

Howard F. Rase, after receiving his B.S. in chemical engineering at the University of Texas in 1942, served as a Chemical Engineer for the Dow Chemical Company, a Process Engineer for Eastern States Petroleum Company, and a Process and Project Engineer for Foster Wheeler Corporation. In 1949, he entered the graduate program in Chemical Engineering at the University of Wisconsin and received his PhD in 1952. He then joined the faculty of Chemical Engineering at the University of Texas, where he served for 45 years, specializing in plant design, catalysis, and process kinetics, and with research emphasis on catalyst characteristics, development, and deactivation. He has written six technical books for professional engineers [*Project Engineering of Process Plants* (with M. H. Barrow), *Piping Design for Process Plants*, *Philosophy and Logic of Chemical Engineering*, *Chemical Reactor Design for Process Plants* (Vols. 1 and 2), and *Fixed-Bed Reactor Design and Diagnostics: Gas-Phase Reactions*] and served as a consultant to industry for 47 years on reactor design, catalysis, and process improvement.



## *Dedication*

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*To my wife Beverly and our granddaughters,  
Carolyn Elizabeth and Kathryn Victoria*





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# How to Use This Handbook

## **Index**

To find information on heterogeneous catalytic processes, use either the index of products or index of reactants. These indices provide a quick access to page numbers at which sections related to a given product or reactant can be found.

## **Table of Contents**

Each chapter covers a specific reaction type along with separate coverage of a number of commercially significant examples. Each of these examples is subdivided in the chapters and in the table of contents in most cases as follows: product uses, reaction chemistry and thermodynamics, reaction mechanism, catalyst type (including suppliers and licensors), process-unit descriptions, and process kinetics. The table of contents provides, therefore, a convenient means for quickly locating specific information in each of the above categories for 150 commercial heterogeneous catalytic processes organized into 19 major reaction types designated as chapters.



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# A Word about Kinetics, Mechanisms, and Thermodynamics

Kinetic equations have been included for each reaction considered when sufficient experimental data warrants the usefulness of the proposed form. Simplicity is preferred, which is often possible over the narrow range of optimum operating conditions used in practice.

A logical mechanism or reaction scheme is also included when available, since it is a valuable tool in reasoning about catalyst performance and improvement. Unfortunately, the development of a reasonable mechanism is difficult and requires sophisticated and tedious observations. In earlier decades, the development of a kinetic expression that fit experimental data was often referred to as *confirming a mechanism*. Such so-called mechanisms were based on a general conceptual framework such as Langmuir–Hinshelwood or Rideal–Eley kinetics. In many cases, these kinetic forms have proved useful in process modeling, but they do not constitute proof of a mechanism. In fact, Power–Law kinetics has, in many cases, been useful in process modeling as well, and generally no mechanistic meaning is assigned.

Unless otherwise noted, thermodynamic data for reactions reported herein as heats of reaction and equilibrium constants were calculated from the tabulations by Stull, Westrum, and Sinke\* of enthalpies and equilibrium constants of formation of the reactants and products in the ideal gaseous state from 298 to 1000 Kelvins. Accurate design calculations must correct for non-idealities for systems deviating from the ideal gaseous state. Modern design programs provide rigorous and readily usable routines for obtaining accurate thermodynamic data over a wide range of conditions.

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\* Stull, D. R.; Westrum, E. F., jr. and Sinke, G. C., *The Thermodynamic Properties of Organic Compounds*.



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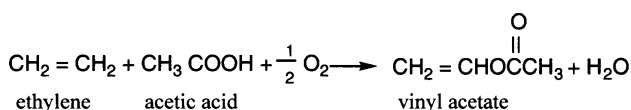
# 1 Acetoxylation

Acetoxylation involves the replacement of hydrogen by an acetate group in an oxygen containing atmosphere and the formation of water. The reaction occurs with vinyl, allyl, benzyl, and aryl hydrogens.<sup>1</sup>

## 1.1 ETHYLENE + ACETIC ACID → VINYL ACETATE

Vinyl acetate consumes the largest fraction of acetic acid manufactured. The major uses of vinyl acetate include homopolymerization to polyvinyl acetate (PVA) used in the production of adhesives, paints, and binders, and it is an important ingredient of water-based paints. The glass transition of PVA is below room temperature, and the painted coating forms a film after the water base evaporates. Copolymers of vinyl acetate and vinyl chloride are used in flooring, and a small amount in PVC pipe.<sup>2</sup> A significant portion of polyvinyl acetate is converted by saponification to polyvinyl alcohol, which is used to produce fibers (Japan) as well as textile sizing, adhesives, emulsifiers, and paper coatings.<sup>2</sup> Polyvinylbutyral is made by reacting butyral aldehyde with the hydroxyl groups in PVA and is used for the inner shatter prevention layer of safety glass.<sup>2</sup>

### CHEMISTRY (VAPOR PHASE)



130–180°C @ 5–12 bar

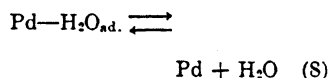
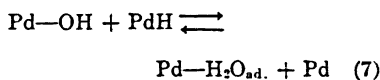
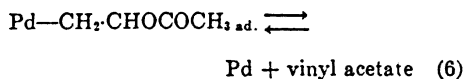
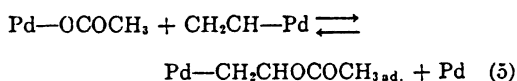
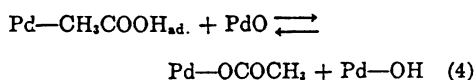
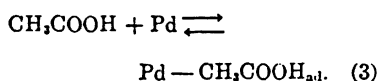
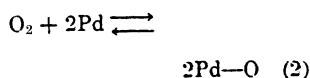
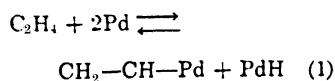
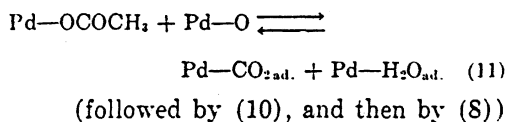
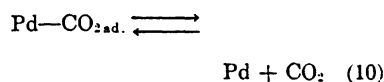
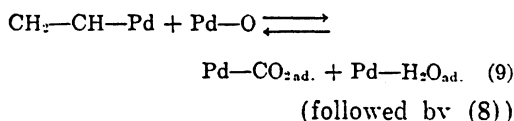
Catalyst: Pd on activated carbon or on silica, or Al<sub>2</sub>O<sub>3</sub> plus promoters (see “Catalyst Types”).

### MECHANISM

Although some studies suggest palladium (II) acetate, Pd<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub>, as the catalytically active species,<sup>5</sup> it appears that the reaction occurs between dissociatively adsorbed acidic acid and dissociatively adsorbed ethylene on palladium.<sup>6</sup> See Figure 1.1.

Detailed proofs of the various steps have not been forthcoming, but the investigators did definitely confirm that Pd<sub>2</sub>(CH<sub>3</sub>CO<sub>2</sub>)<sub>2</sub> was not an active species. In fact, catalytic activity is maintained only in those conditions where Pd(II) acetate does not exist.<sup>7</sup> Such conditions are low partial pressures of acetic acid and oxygen, higher temperatures, and addition of potassium acetate solution to the feed.<sup>7</sup> Apparently, Pd(II) acetate is associated with aggregation of palladium and ultimate deactivation.



*Main reaction**Side reaction*

**FIGURE 1.1** Proposed Mechanism for Vapor-Phase Catalyzed Synthesis of Vinyl Acetate from Ethylene. Reprinted by permission: Nakamura, S., and Yasui, T., *Journal of Catalysis* 17, 366 (1970), Academic Press, Inc.

**CATALYST TYPES AND LICENSORS**

The two major processes in use (Bayer/Hoechst and Quantum) differ primarily in the preparation of the proprietary catalysts. Both employ palladium along with alkali metal acetates on silica alumina or on activated charcoal. The Bayer/Hoechst catalyst is prepared by depositing a Pd salt on the carrier followed by reduction to the metal, whereas the Quantum catalyst is prepared by depositing palladium acetate on the carrier.<sup>3,4</sup> In addition to alkali acetates, both catalysts contain promoters variously reported as cadmium, platinum, rhodium, and gold.<sup>3,4</sup> The catalyst is produced in the form of tablets or extrudates depending on the nature of the carrier. A fluidized catalyst was introduced by BP Chemicals (London) in late 1998. See “Process Units.”

**CATALYST DEACTIVATION**

Traces of acetylene in the ethylene feed is a strongly adsorbed poison, but the catalyst can be reactivated by oxygen treatment.<sup>6</sup>

The alkali acetates incorporated in the catalyst, which promote activity and selectivity, migrate in the direction of flow and must be renewed over an operational cycle to reach run times of 2-1/2

to 3+ years.<sup>3,4</sup> Renewal is accomplished by addition of these salts in solution via the gaseous feed to the reactor.

## PROCESS UNITS

These processes were introduced in the late sixties and many improvements have been made by various operators. Such actions are not in the public domain, but the general operating procedure has been described<sup>3,4,6</sup>.

The exothermic reaction, like so many partial oxidations, is carried out in a fixed bed multitubular reactor. Boiler feed water is used as the shell-side fluid. Operating conditions are reported to be in the range 140–180°C, and pressure is in the range of 5 to 12 bar. Although the reaction rate increases with pressure, higher pressures force the flammability limit to lower oxygen content and thus lower conversion to vinyl acetate. Hence, an optimum pressure is constrained by the catalyst characteristics and the flammability of the feed mixture.

Feed to the reactor is composed of fresh feed plus recycle. A typical reported total feed in mole percent is 10–20% acetic acid, 10–30% CO<sub>2</sub>, and 50% ethylene.<sup>4</sup> The remainder is oxygen, which is fed at 1.5% below the flammability limit, which varies with operating conditions for a particular unit. Operating temperature also affects efficient energy recovery. A low temperature may only provide preheat for boiler feed water, while a higher temperature can produce a more useful saturated steam.

Ethylene that is fed in excess reaches conversions of only 8–10%, while oxygen conversion is in the range of 90%.<sup>4</sup> Acetic acid conversion is up to 30%. The total yield, which accounts for recycled acetic acid, is reported as high as 99%.

Product gas is cooled and the condensate consisting of vinyl acetate and water product is readily separated in a two-phase separator drum. The crude vinyl acetate is then piped to a distillation section for purification. The remaining vapor phase is washed, and then CO<sub>2</sub> is removed in a potash solution, followed by recovery and recycling of a portion of the CO<sub>2</sub>, which is valuable for temperature and reaction control.

In late 1998, BP Chemicals (London) introduced a fluid-catalyst process (LEAP) using a similar chemistry but having the usual fluidized-bed advantage of precise temperature control and ease of catalyst regeneration. Lower investment costs and longer sustained catalyst activity are claimed. Operating conditions are 150–200°C at 8–10 bar, and yield is 99% on acetic acid and 92–94% on ethylene.<sup>15</sup>

## PROCESS KINETICS

Based on the mechanism shown in Figure 1.1, kinetic data were fit using a rate determining step of the combination of dissociately adsorbed ethylene and acetic acid.<sup>6</sup>

The rate of vinyl acetate formation is

$$R_{VAC} = \frac{k_5 K_1 K_2^{0.5} K K_4 p_{C_2H_4} p_{O_2}^{0.5} p_{CH_3COOH}}{[1 + K_1 p_{C_2H_2} + (K_2 p_{O_2})^{0.5} + K_3 p_{CH_3COOH}]^2}$$

where  $p = \text{atm}$

$R_{VAC} = \text{g/l hr}$

This complex multiconstant equation should be amenable to simplification for the commercial operating range.

## 1.2 BUTADIENE + ACETIC ACID $\rightarrow$ 1,4-DIACETOXY-2-BUTENE $\rightarrow$ 1,4-BUTANEDIOL $\rightarrow$ TETRAHYDROFURAN

The production of 1,4-butanediol is possible by several different routes. In the U.S.A. and Europe, the Reppe acetylene process continues to dominate because of the use of  $C_4$  hydrocarbons for other profitable products. In Japan, however, acetoxylation of butadiene is the preferred process step to 1,4-butanediol and tetrahydrofuran. The major uses of 1,4-butanediol include the production of tetrahydrofuran and polyesters. Tetrahydrofuran is an excellent solvent for a wide variety of polymers and is also used in the manufacture of polytetramethylene glycol, which is an important reactant in forming certain polyurethanes and stretch fibers.

The polyester, polybutene-terephthalate, is formed by the polymerization of 1,4-butanediol with terephthalic acid. It is more flexible than polyethylene terephthalate and is used for injection molding applications.

### CHEMISTRY (LIQUID PHASE)

Unlike the Reppe process, which primarily produces 1,4-butanediol, a portion of which can be converted to tetrahydrofuran, the acetoxylation process unit can be operated to produce both 1,4-butanediol and tetrahydrofuran (THF) from the same intermediate (1,4-acetoxyhydroxybutane). The relative amounts of each can be adjusted by changes in operating temperature and residence time.<sup>3</sup>

The acetoxylation intermediate is hydrogenated and then hydrolyzed to produce the desired products<sup>9,10,11,12</sup> as depicted in Figure 1.2.

### CATALYST TYPE

The proprietary acetoxylation catalyst is palladium on activated charcoal promoted by tellurium. It is reported to be in the form of granules, probably  $4 \times 8$  mesh. The hydrogenation step employs a standard hydrogenation catalyst, either supported nickel or palladium. In the case of nickel, zinc or some other additive may be added to moderate activity. The hydrolysis reactions are catalyzed by specially prepared cation and anion-exchange resins.<sup>12</sup> Diacetocyclization is catalyzed by a cation-exchange resin. Other acetoxylation catalysts have been described, including Pd-Sb-V-CsCl-KOAC.<sup>14</sup>

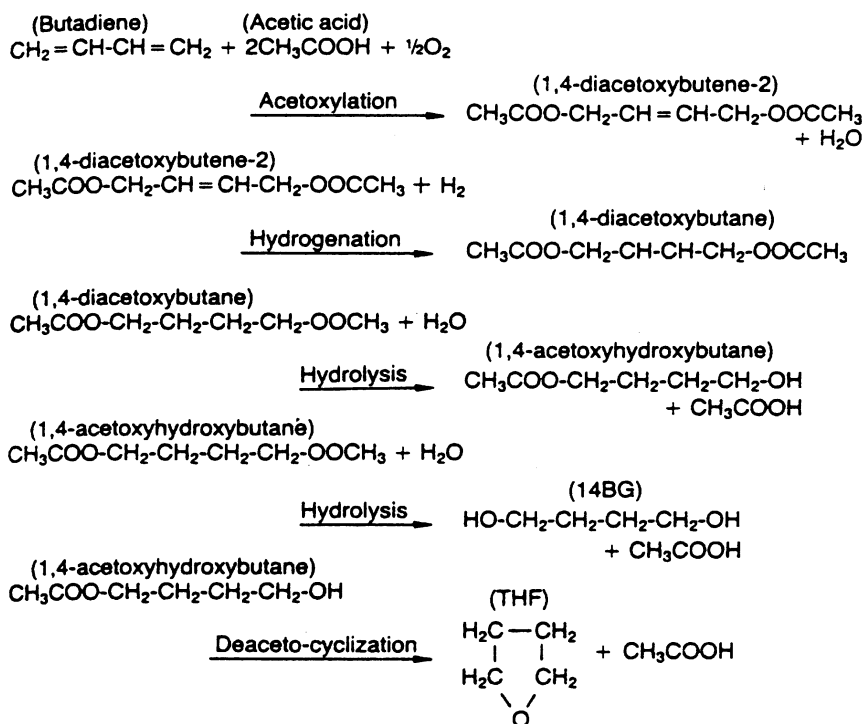
### Licensors

The licensor is Mitsubishi-Kasei Corporation.

### CATALYST DEACTIVATION

Catalyst life for the acetoxylation catalyst is one year, but the catalyst can be regenerated after removal by treatment with oxidation and reducing agents.<sup>12</sup> Although some polymerization of butadiene could be expected, it is minimized by the liquid feed acting as a useful wash of polymer as it is formed. The high activity of the catalyst was made possible the use of moderate temperatures that avoided excessive coking and assured the best selectivity. The catalyst promoted with CsCl and KOAC exhibits movement of these components after long use, which reduces the resistance to coke formation that these components provide.<sup>14</sup>

Activated charcoal proved to be the best catalyst carrier. It was not adversely affected by acetic acid and did not produce significant amounts of high boilers.<sup>10</sup>



**FIGURE 1.2** Reaction Scheme for the Production of 1,4-Butanediol and Tetrahydrofuran via Acetoxylation. Basis: Mitsubishi Chemical Ind. 14 BG/THF process. Reprinted by permission: Tansabe, Y., *Hydrocarbon Processing*, p. 189, Sept. 1981.

## PROCESS UNITS<sup>9-12</sup>

The acetoxylation reactor is a fixed-bed reactor that operates at 70°C and 70 bar. Butadiene, acetic acid, and air are mixed and fed together. The air feed rate is adjusted to maintain a safe non-flammable mixture. Recycled acetic acid removed from the product stream provides an additional heat sink for temperature control. Acetic acid is removed from the 1,4-diacetoxybutene-2 product by distillation, and the 1,4-diacetoxybutene-2 is hydrogenated in a trickled-bed. The 1,4-diacetoxybutane is then hydrolyzed over the ion-exchange resins to 1,4-acetoxy-hydroxybutane (a monoacetate) and 1,4-butanediol at 60°C and 50 bar. The ratio of these two products can be changed by adjusting operating conditions.

After removing the excess water and acetic acid by distillation, a second stage of hydrolysis is practiced to improve yields by reacting the remaining diacetate. Excess water is again removed by distillation, followed by a distillation that separates the monoacetate from the 1,4-butanediol. The butanediol is purified and the monoacetate sent to the diaceto-cyclization step to produce tetrahydrofuran. The combined yields of 1,4-butanediol and THF based on diacetoxybutane fed is 99%. The yield of 1,4-diacetoxybutene-2 is 90% based on butadiene fed and the yield of diacetoxybutane is 98% based on diacetoxybutene fed.<sup>12</sup>

## PROCESS KINETICS

Extensive studies in the vapor phase on Pd catalyst with various promoters have revealed that minimal adsorption of butadiene favored the desired reaction because coke formation was thereby

inhibited.<sup>14</sup> In such cases, the rate of reaction in the vapor-phase process tends to be proportional to the acetic acid and oxygen partial pressures. The reduction in coke formation is further advanced in the liquid-phase process because of the washing effect of the liquid reactants, particularly butadiene. It is reasonable to assume that the rate for the liquid-phase process will also be proportional to acetic acid concentration and oxygen partial pressure.

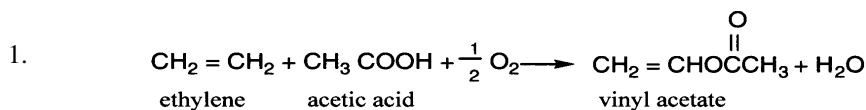
### 1.3 PROPYLENE + ACETIC ACID → ALLYL ACETATE → ALLYL ALCOHOL

Acetoxylation is one of several reaction paths for the manufacture of allyl alcohol. The once-dominant process, alkaline hydrolysis of allyl chloride, is disappearing because of its corrosive environment and the large amount of by-product, NaCl, that must be disposed of or recovered for chlorine. The acetoxylation process, by contrast, produces the same amount of acetic acid as is used in the reaction.

Allyl alcohol major uses have been as the feedstock in the production of glycerol, and diethylene glycol bis(allyl carbonate) for optical lenses.<sup>3,13</sup> Also, allyl alcohol esters are used in polymers, and allyl alcohol is used to produce epichlorohydrin and in an alternate route to 1,4-butanediol.<sup>3,13</sup>

#### CHEMISTRY (VAPOR PHASE)

The acetoxylation reaction to the acetates is analogous to the vinyl-acetate process, except propylene is used rather than ethylene.



150–250°C @ 5–10 bar

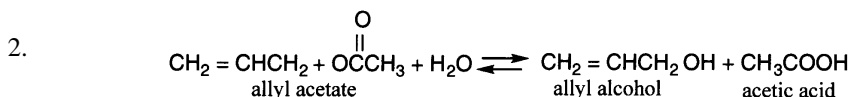
Catalyst: Pd on activated charcoal

$\Delta H = -45$  kcal/mole

Liquid phase hydration

60–80°C

Catalyst: acidic ion-exchange resin



Liquid phase hydration

60–80°C

Catalyst: acidic ion-exchange resin

#### MECHANISM

See section on “Vinyl Acetate” process.

## CATALYST TYPE

The catalyst is similar to that used for vinyl acetate production. It is palladium along with an alkali metal acetate deposited on activated charcoal. Promoters are reported to be iron or bismuth compounds.<sup>3</sup>

## Licensors

Licensors are Showa Denka, Daicel Chemical Industries, Hoechst, and Bayer.

## CATALYST DEACTIVATION

Propylene feed stocks often come from steam cracking units and can contain small amounts of acetylene due to upsets in the selective hydrogenation of acetylene impurities at the cracking unit. Acetylene is a strongly adsorbed poison, but the catalyst can be reactivated by oxygen treatment.

## PROCESS UNIT

The acetoxylation is accomplished in the vapor phase in a fixed-bed reactor, probably a multitubular reactor with cooling by boiler feed water, since the operating temperature is such that valuable steam can be produced. Operating conditions are variously reported as 150–250°C, depending on the process.<sup>3,13</sup> See the description of the vinyl acetate process for more analogous detail.

The hydrolysis to allyl alcohol is done using the cooled liquid phase separated from the allyl acetate reactor effluent. The reactor is an adiabatic fixed-bed unit packed with the acidic ion exchange resin in the form of granules.

## PROCESS KINETICS

It is reasonable to suggest that a similar kinetic expression as used for vinyl acetate might apply.

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# 2 Alkylation

## 2.1 INTRODUCTION

The term *alkylation* refers to the replacement of a hydrogen atom bonded to a carbon atom of a paraffin or aromatic ring by an alkyl group.<sup>1</sup> Most alkylations are acid catalyzed either by a homogeneous liquid strong-acid catalyst ( $\text{H}_2\text{SO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{HF}$ ,  $\text{AlCl}_3$ ) or a solid strong-acid, which has been used where feasible and economical (zeolites, supported acids, acidic ion-exchange resins). Developments with heterogeneous catalysts were driven, in part, by efforts to minimize waste disposal problems associated with spent acids. Not all alkylation processes, however, have been amenable to the use of a heterogeneous acid catalyst which, in some reaction systems, produces coke at a rapid rate. Thus, the production of alkylate gasoline from isobutane and olefins continues to employ either liquid sulfuric or hydrofluoric acid. Major improvements in handling and reducing acid consumption, and thus waste acid quantities, have proved successful in such processes.<sup>1</sup>

### 2.1.1 SOLID ACID-CATALYST MECHANISM

The mechanistic concepts for solid-acid catalysts derive largely by analogies from the many studies on homogeneous acid catalysis which present a more readily verifiable system for detailed study. In recent years various studies on solid catalysts using, for example, deuterium exchanged reactants have confirmed many of the earlier analogies. The steps shown in Figure 2.1 present a reasonable mechanism for benzene alkylation by ethylene that is applicable to other similar alkylations.<sup>2</sup> The first step shows the formation of the carbenium ion by chemisorption of ethylene on an active Brønsted site. This step rapidly reaches an equilibrium concentration of surface carbenium ions. The second step is the reaction of the benzene ring with the surface carbenium ion, and this is the rate controlling step. The third step involves the desorption of the product alkylated benzene and the regeneration of the Brønsted acid site. This third step is also rapid and at equilibrium.<sup>2</sup>

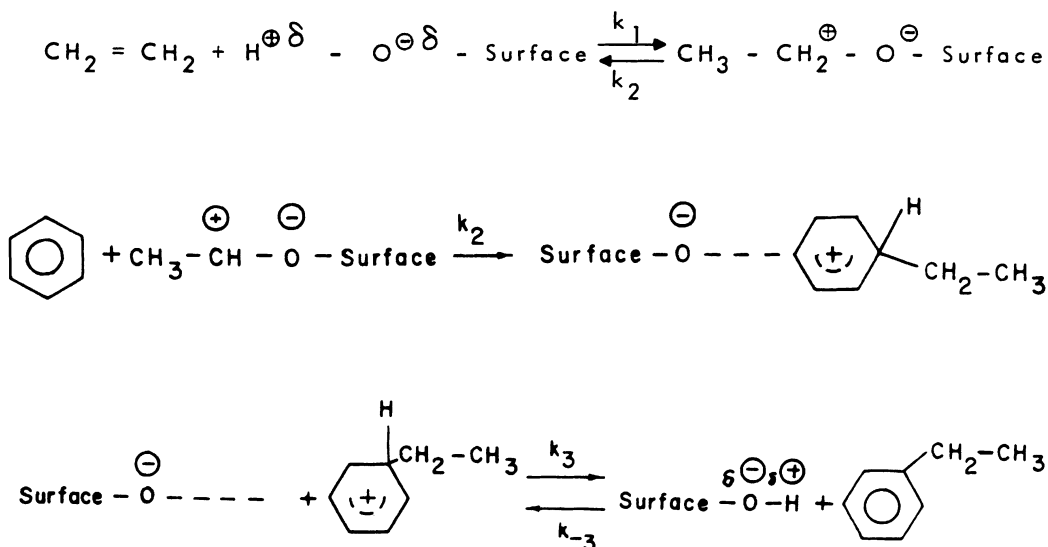
Figure 18.26 (Chapter 18) illustrates qualitatively the relative strengths of acid sites for the several carbenium ion reactions.<sup>2</sup> Alkylation and cracking require the same level of high acid strength, which is not surprising, since alkylation is the reverse reaction of cracking. Cracking is endothermic and requires high temperatures, whereas alkylation is exothermic and requires low temperatures (below  $400^\circ\text{C}$ ). Thus, alkylation can be made exclusive by low-temperature operation. However, low temperature favors polymerization and catalytic coke formation, which can be suppressed by catalysts with low coke forming tendencies.

Alkylation of benzene by higher olefins such as propylene are more easily accomplished because the secondary carbenium ion is more reactive. Hence, lower-temperature operation is possible.

### 2.1.2 CATALYST TYPES AND USES

The various solid catalysts that are used or that have been used are summarized in Table 2.1. Additional details will be found under the several process descriptions following this section.





**FIGURE 2.1** Mechanism for Ethylbenzene from Ethylene and Benzene by Solid Alkylation Catalysts. Equations reproduced from Wojciechowski, B. W. and Corma, A., *Catalytic Cracking: Catalysts, Chemistry, and Kinetics*, Marcel Dekker, New York, 1986, by courtesy of Marcel Dekker, Inc.

### 2.1.3 THE ROLE OF ZEOLITES IN ALKYLATION

Traditional acid-catalyzed alkylations involve liquid acids or solid supports impregnated with acids such as phosphoric acid. These processes, although efficient, can cause corrosion and create major disposal problems. By contrast zeolites create no environmental problems and, in fact, 34 naturally occurring zeolites make up a major portion of the Earth's crust. This environmentally neutral character of zeolites certainly made them a potentially valuable catalyst in the acid form. But the discovery of shape selectivity of zeolites gave catalyst development chemists another tool for optimizing catalyst characteristics.

The literature on zeolites is massive, and no attempt will be made here to summarize the fascinating detail of the science and engineering of zeolite catalysis. The following major issues, however, deserve the reader's attention.

#### Shape Selectivity

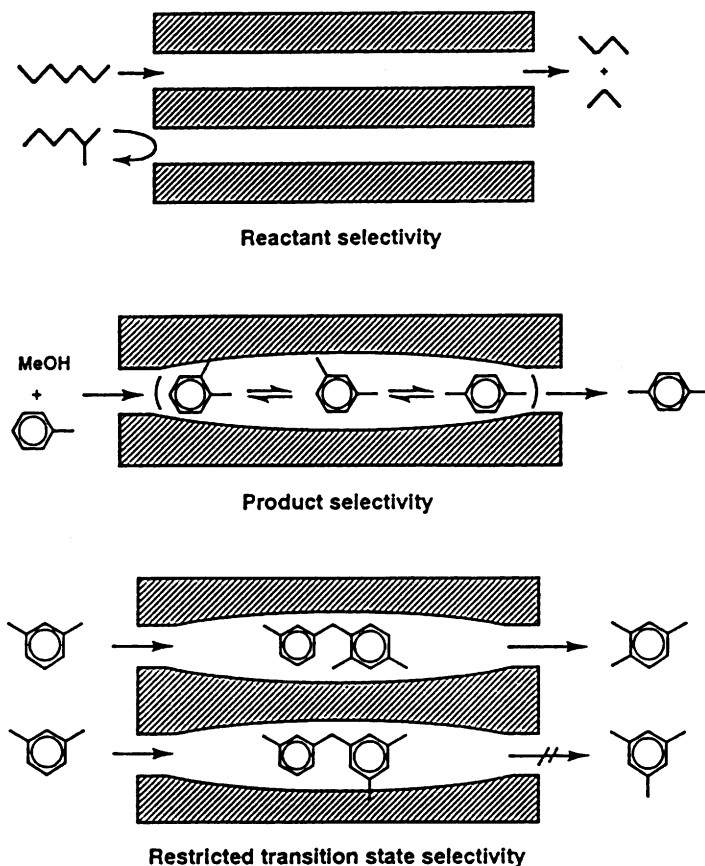
Shape selectivity can be attained by a variety of procedures. See Figure 2.2.<sup>7,8</sup>

- *Molecular exclusion (reactant selectivity)*. Select a zeolite with pore size and structure such that some of the molecules in the reactor feed can enter the pores and react, and others cannot.
- *Molecular exclusion (product selectivity)*. Select a zeolite with opening pore size and inner pore size such that one or more of the products is too bulky to diffuse out of the cavity. The other products readily diffuse out. Those remaining behind may crack to smaller molecules or form coke that deactivates the catalytic surface.
- *Transition-state selectivity*. Select a zeolite with an inner space of a size that is inadequate for a particular transition state but adequate for another, thereby favoring one product over another.

**TABLE 2.1**  
**Solid Alkylation Catalyst Types and Uses\***

Catalyst	Description	Suppliers	Licensor	Uses
Boron trifluoride on $\gamma$ - $\text{Al}_2\text{O}_3$	Small amount of $\text{BF}_3$ on alumina	UOP LLC	UOP LLC (Alkar Process)	Alkylation of benzene with ethylene (vapor-phase process) to produce <b>ethylbenzene</b>
Zeolite, Y-type (faujasite)	USY-type (ultra stable) pore size: 7.4 Å $\text{SiO}_2/\text{Al}_2\text{O}_3 > 3$	UOP LLC	(original catalyst developed by Unocal)	Alkylation of benzene with ethylene (liquid-phase process) to produce <b>ethylbenzene</b>
Zeolite, ZSM-5 (pentasil)	Specially modified medium pore zeolite high silica/alumina ratio ( $>20$ ) pore size: 5.5 Å extrudates	Mobil	Mobil-Badger, (now Mobil-Raytheon Engineers & Constructors) (Third Generation EP Process)	Alkylation of benzene with ethylene (vapor-phase process) to produce <b>ethylbenzene</b>
EBMAX or EBEMAX catalyst	MCM-22 pentasil zeolite extrudates	Mobil	Mobil-Raytheon Engineers & Constructors (EBMAX)	Alkylation of benzene with ethylene to produce <b>ethylbenzene</b> (liquid-phase)
Packaged zeolite	Pentasil zeolite packaged	United Catalysts CDTECH	ABB Lummus Global	Catalytic distillation simultaneous alkylation of benzene with (ethylene or propylene) to produce <b>ethylbenzene</b> or <b>cumene</b>
Phosphoric Acid on Kieselguhr (SPA Process, i.e. solid phosphoric acid process)	65-70% $\text{H}_3\text{PO}_4$ -n-silica. Extrudates: 1/4 and 3/16-in. spheres: 1/4 $\times$ 5/16 in., 3/16 $\times$ 1/4 in. beta zeolite extrudates	United Catalysts UOP LLC	UOP LLC (SPA Process i.e. solid phosphoric acid process)	Alkylation of benzene with propylene (vapor-phase process) to produce <b>cumene</b>
Q-Max catalyst		UOP LLC	UOP LLC	Alkylation of benzene with propylene to produce <b>cumene</b> (liquid-phase)
MCM-22 catalyst	Pentasil zeolite extrudates	Mobil	Mobil-Raytheon Engineers & Constructors	Alkylation of benzene with propylene to produce <b>cumene</b> (liquid-phase)
3-DDM	Dealuminated mordenite to create controlled 3-dimensional structure	Dow	Dow/Kellogg	Alkylation of benzene with propylene to produce <b>cumene</b> (liquid-phase)
Solid-acid catalyst (not revealed)	Heterogeneous acid catalyst	UOP LLC	UOP (Detal Process)	Alkylation of higher molecular-weight olefins with benzene to produce <b>linear alkyl-benzenes</b> for detergent manufacture

\*Based on information from Refs. 1 and 3-6. All of these catalysts are proprietary. Only limited information on catalyst details exists in the open literature, and some such information is speculative.



**FIGURE 2.2** Mechanism of Shape-Selective Catalysis. Reprinted by permission: Sugi, B. Y. and Kubota, Y., *Catalysis: Specialized Periodical Reports*, Vol. 13, p. 56, The Royal Society of Chemistry, Cambridge, England, 1997.

- *Configurational diffusion controlled selectivity.* Select a zeolite of such structure that a large difference exists between rapidly diffusing reactant and product molecules and other molecules present that diffuse much more slowly. The slower diffusing molecules can thus become only minor players in the reaction process.

Many other shape-selective attributes have been postulated and have been reviewed.<sup>8</sup>

### Modification of Zeolites<sup>8,9</sup>

In the production of synthetic zeolites, the catalyst developer has several tools for modifying characteristics of a zeolite to fit the needs of a desired catalyst system. More detailed discussions are available, but the following provides a brief review.

- $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio  
The ratio can be modified by chemical dealumination or by steaming, which removes framework aluminum. The steaming process when properly applied can develop mesopores that facilitate the diffusion of larger molecules.

- Crystallite Size

Crystals can be made smaller by various techniques, including lower temperature in the presence of saccharides or by thermal shock. Large crystallites are favored by low-speed agitation and longer crystallization time. Lower crystallite size increases rate of diffusion.

- Substitution of other Atoms in the Framework

Other atoms (B, Cr, Ga, Ge, Fe, P, and Ti) have been substituted for either Al or Si atoms during synthesis or post synthesis modification. A variety of different properties can be attained.

- Cation-Ion Exchange

Synthetic zeolites are mostly produced with Na or K cations occupying the cation positions. Acid catalysis requires that these cations be replaced by hydrogen protons. In the manufacturing process, this ion exchange is accomplished following spray drying using a 5–10% ammonium chloride or nitrate solution. This step is followed by drying and calcining in an inert gas during which  $\text{NH}_3$  is released, leaving behind acid sites ( $\text{H}^+$ ) referred to as the hydrogen form (e.g., ZSM-5  $\rightarrow$  HZSM-5). If organic compounds are used in preparation of the initial zeolite, they must be removed by calcining prior to ammonium exchanges.

- Binders

Both zeolite catalysts and adsorbents are combined with a binder, usually a clay such as halloisite, montmorillonite, or attapulgite. The clay in gel form is mixed with 10–20% of zeolite as a paste and then spray dried. The porosity of the binder is greater than the zeolite and does not, in most cases, limit the net rate of diffusion to the active sites on the zeolite.

- Pore Size

Pore size can be manipulated by post-synthesis procedures such as depositing organo-silicones in the pore structure to alter the diffusivity differences between isomers such as the xylenes so that one isomer (p-xylene) will have a much greater diffusivity than the larger o-xylene or m-xylene. Treatment with phosphorus, which attaches to the zeolite active acid site via the framework oxygen, has been used to reduce the effective pore size of the channels and pore openings of ZSM-5 and thus produces a p-xylene selective catalyst.<sup>8</sup>

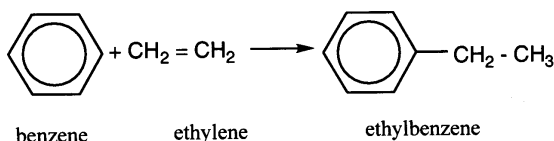
## 2.2 ALKYLATION OF BENZENE AND TOLUENE

### 2.2.1 BENZENE + ETHYLENE $\rightarrow$ ETHYLBENZENE

All but about 1% of ethylbenzene is used for dehydrogenation to styrene. The remaining small amount is primarily used as a solvent for some types of paint. Essentially, all ethylbenzene is produced by alkylation of benzene with ethylene. A small amount is also produced from mixed xylenes by superfractionation, which is highly energy intensive.

#### Chemistry

##### Main Reaction



Temp., K	$\Delta H$ , kcal	$K_p$
500	-24.97	$24.668 \times 10^3$
600	-24.83	$33.729 \times 10^2$
700	-24.66	17.378
800	-24.48	1.914

### Operating Conditions<sup>1,5,11,12</sup>

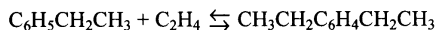
Process	Catalyst	Temperature	Pressure
Alkar (vapor phase), UOP LLC, (process no longer offered)	BF <sub>3</sub> /alumina	100–150°C	25–35 bar
Lummus-UOP (liquid phase)	USY zeolite extrudate	≈270°C	38 bar
Mobil-Badger* (vapor phase)	ZSM-5 zeolite extrudates	400–450°C	15–30 bar
EB-MAX (liquid phase), Mobil/Raytheon	MCM-22 extrudates	not reported	
Catalytic Distillation, ABB Lummus, Global	packaged zeolite	not reported	

\*Depending on plant economics, temperatures as low as 350°C and pressure as low as 8 bar may be used.

### Side Reactions

The following side reactions are possible:

- *Polyethylbenzenes*. A portion of the ethylbenzene formed is further alkylated to di-, tri-, tetra-, etc. benzenes.

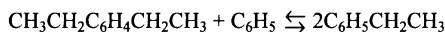


ethylbenzene          ethylene          diethylbenzene

$$\Delta H = -23.46 \text{ kcal @ } 600^\circ\text{K}$$

$$K_p = 19.543 \text{ @ } 600^\circ\text{K}$$

- *Transalkylation*. Polyethylbenzenes are converted to ethylbenzene and benzene.



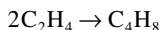
diethylbenzene          benzene          ethylbenzene

$$\Delta H = 1.38 \text{ kcal @ } 600^\circ\text{K}$$

$$K_p = 17.022 \text{ @ } 600^\circ\text{K}$$

By using an excess of benzene, transalkylation is favored.

- *Oligomerization*. This polymerization-type reaction is the most unwanted reaction, since the oligomers are precursors to other by-products, the most deleterious of which is coke formation.



$$\Delta H = -17.49 \text{ kcal @ } 600^\circ\text{K}$$

$$K_p = 144.5 \text{ @ } 600^\circ\text{K}$$

The oligomers can also alkylate benzene, producing higher alkylbenzenes. Coke formation by oligomer reactions constitutes a reaction pathway that can lead to catalyst deactivation. Other possible side reactions include cracking of oligomers, dehydrogenation, and isomerization.<sup>5</sup> Process improvements have focused strongly on minimizing such undesired reactions.

Other side reactions that occur to some degree are isomerization ( $\text{EB} \rightarrow \text{xylenes}$ ), dehydrogenation, and other alkylations. Many of the products of these reactions occur only in very small amounts. Benzene feed often contains small amounts of toluene (seldom over 1000 ppm). It, of course, is alkylated and becomes dealkylated in the transalkylation reactor. Toluene then becomes part of the ethylbenzene product, but it causes no problem in the subsequent styrene-producing process. Xylene impurities in the product ethylbenzene are much lower than produced in the  $\text{AlCl}_3$  process.

### Mechanism

See Figure 2.1.

### Catalyst Suppliers and Licensors

See Table 2.1. The catalysts are proprietary and the processes are licensed. Limited information on catalysts details exists in the open literature.

#### *Yield and Purity*

The overall yield for most of these processes is in the range of 98.5–99.5, and product purity is reported as high as 99.9%.

### Catalyst Deactivation

The major deactivating agent is coke. Coke formation is inhibited by the relatively narrow pores of zeolites used in alkylation reactions. The limited space in the channels provides less space for the formation of large coke precursor molecules. Of course, coke formation is catalyzed by acid sites, and some attempt to optimize acid strength is a possible procedure for reducing coke-forming reactions.<sup>13</sup>

Organic nitrogen compounds, being strong bases, will poison zeolite and other acid catalysts.

### Catalyst Regeneration

When necessary, coke may be removed by carefully burning it in an air-nitrogen mixture. Great care must be exercised, especially if water vapor as steam is present, since there is danger in it destroying some of the zeolite crystallinity.<sup>12</sup> Licensors' recommendations must be carefully followed.

### Process Units<sup>1,6,11,12</sup>

Until about 1980, most ethylbenzene plants were based on the homogeneous catalysis of aluminum chloride. The process was successful but had the disadvantage of a highly corrosive liquid system requiring expensive lined or Hasteloy reactors. Spent catalyst had to be washed and neutralized and then disposed, which action is becoming increasingly costly and has fueled the efforts to develop noncorrosive catalyst systems involving solid catalysts. Few new  $\text{AlCl}_3$ -based plants have been built since 1980, and none since 1990, but 40% of EB plants continued to use their  $\text{AlCl}_3$  catalyzed alkylation.

Vapor-phase processes with solid catalysts can use dilute ethylene streams and have adequate ethylene concentration at the catalyst surfaces. Essentially pure ethylene, of course, can be used, and most vapor-phase plants use polymer-grade ethylene.

#### *Alkar Process (Vapor Phase)*

The first such process using a solid catalyst was developed as early as 1958. It employed a catalyst composed of alumina with boron trifluoride adsorbed on its surfaces in relatively small amounts. This system is not corrosive, but even small amounts of water in the feed will not only tend to remove  $\text{BF}_3$  from the catalyst but will also create a corrosive mixture over time. The catalyst is susceptible to poisoning by CO, sulfur compounds, oxygenates, and water, all of which can be present in dilute refinery ethylene streams and must be removed prior to use. The process proved advantageous for the use of dilute refinery streams (8–10% ethylene) attaining 100% ethylene conversion and 99%+ yields.

A multitubular reactor was used with shell-side cooling. Benzene feed was dehydrated and combined with the ethylene containing steam along with make-up  $\text{BF}_3$  to replace that lost continuously from the catalyst. The recovery section removed carry-over  $\text{BF}_3$  from the reactor product, separated benzene for recycle to the reactor and as feed to the transalkylation reactor for conversion of polyethylbenzenes, (separated from the reactor product), to ethylbenzene. Yields were in the 99%+ range and product purity was typically 99.95 ethylbenzene.

The last plant was built in 1979, and some have been revamped using other processes. The process was unique and highly successful, but waste disposal became an increasingly expensive problem. As the grandfather of solid-catalyst alkylation, it started a major new trend in the industry.

#### *Mobil/Badger ZSM-5 Process (Vapor Phase)*

The original ZSM-5 process was the first zeolite process for alkylation of aromatics (first plant in 1981). It, in many ways, revealed the value of shape selectivity made possible by synthetic zeolites. The medium pore-size zeolite (ZSM-5) proved ideal for avoiding or minimizing undesired reactions such as oligomerization and also exhibited only a minor effect on product yield and quality when nonaromatics are present in the feed to the reactor.

Initially, two reactors were provided so that coke could be removed by burning in a used bed while flow is switched to the second bed. Over time, changes in operating procedures, and probably zeolite synthesis, along with zeolite post-synthesis modifications, have culminated in the third-generation process that uses only one alkylation reactor, since time between regenerations is now two years rather than only several months.

Briefly, the vapor-phase process consists of a main multitubed adiabatic reactor with cold-shot cooling between beds. Fresh benzene and recycle benzene are combined and preheated in a furnace. This heated stream then flows to the reactor inlet where it is joined by a portion of the ethylene that has not been heated. The remainder of the ethylene is introduced between the beds to control the bed temperature. At higher temperatures, the reverse reaction of dealkylation becomes favorable (e.g., above 600°C), as do other undesired reactions.

Excess benzene is used in a ratio of 5:1 benzene-to-ethylene (values up to 20 have been reported) to reduce the tendency to form additional amounts of polyethylbenzenes. Excess benzene also favors transalkylation.

Reactor effluent flows to the purification system where excess benzene is separated overhead in the first column and recycled to the main reactor. The bottoms flows to an ethylbenzene column where ethylbenzene is separated overhead, and the bottoms flows to a polyethylbenzene (PEB) column where PEB is separated overhead and sent to a smaller reactor for transalkylation to ethylbenzene from which water and light materials are stripped prior to recycling to the first column.

The original design provided for direct recycle of polyethylbenzene to the main reactor where transalkylation can also be accomplished. The third-generation design provided a separate transalkylation reactor. Although the same catalyst is effective for both alkylation and transalkylation, separate operating conditions for transalkylation improve the reaction efficiency. Generally, a higher operating temperature for transalkylation is indicated for operating conditions for the main reactor. Higher alkylbenzenes such as  $C_8$  and  $C_9$ , if formed, reach equilibrium and are simply recycled with the PEB stream. The catalyst is active in decomposing nonaromatics to light gases, which are easily purged. Also, branched-chain alkylbenzenes such as cumene are easily dealkylated, thereby recovering the benzene. Bottoms from the PEB column is small in quantity and is generally used as fuel.

Since the vapor-phase process must operate at a higher temperature, benzene reactor feed must be preheated in a furnace. Vapor-phase operation, however, allows for the use of less costly refinery stream with 10–15% ethylene, which would require high pressures for liquid-phase operation. The only purification required of such streams is the removal of higher olefins that will alkylate and reduce EB yield. Most plants use high-purity ethylene with ethane no higher than 2000 ppm as the impurity. Fortunately, ethane causes no problem in the process and remains inert and is removed with the off gases.

#### *Mobil/Raytheon E&C, EB Process, EBMAX (Liquid Phase)*

Dilute ethylene streams cannot be used for liquid-phase processes, because complete dissolution of ethylene is not possible at economical operating conditions with low gas-phase ethylene partial pressures.

This is a new process, with the first plant commissioned in 1995 by Raytheon Engineers and Constructors (the former Badger component of Raytheon) using a new Mobil catalyst named by Mobil MCM-22. Because the process is operated in the liquid phase, lower temperatures are used, and a preheating furnace is not required. This unique catalyst has a high alkylation activity but does not catalyze oligomerization or cracking. These characteristics make it possible to operate at a lower benzene-to-ethylene ratio with obvious savings in energy costs and lower equipment sizes for both reactors and distillation towers. The layout of the plant is similar to that described above for the Mobil/Badger third-generation process with a multitbed adiabatic reactor and a transalkylation reactor for converting recycled polyethylene benzenes to ethylbenzene.

Since oligomerization does not occur, aliphatic impurities are negligible in the product. Amounts of  $C_8$  and other heavier impurities are very low.

#### *Lummus/UOP EB Process (Liquid Phase)*

This process was developed by Unocal in the 1980s and was the first zeolite-based liquid-phase process. An ultrasensitive USY-type zeolite is used. It is now licensed by ABB Lummus Crest and UOP, and the first plant was built in 1990.

The recovery section is similar to that described for previously described EB processes based on zeolites. Two dual-bed reactors are operated in series with ethylene cold-shot cooling between beds and an intercooler between reactors. The operating temperature (270°C) is close to the critical temperature to take advantage of the higher catalyst activity. Water, however, is added to the feed stream to reduce the tendency to form oligomers.

The product EB is low in xylenes but, as is the case in all these processes, higher aromatics must be removed as residue, which lowers yield, depending on the quantity formed. Careful operation, however, in accordance with licensor recommendations can reduce the net residue production.

#### *CD Tech/ABB Lummus Global and Chemical Research & Licensing (Two-Phase Process)*

This process involves catalytic distillation, which has proved to be the preferred process for the manufacture of MTBE (methyl tert-butyl ether, the gasoline additive). Catalyst is loaded into fiber-



glass cylindrical containers or bales and placed in a pattern in a column so that liquid flows down through the bales and ethylene vapor moves upward. Since oligomerization is a higher-order reaction for ethylene than alkylation, the distillation action causes a lower concentration of ethylene in the liquid. In so doing, oligomerization is retarded, and large excesses of benzene, which accomplishes the same result in other processes, can be avoided. The lower ethylene concentration, however, also retards the main reaction to ethylbenzene and requires more catalyst loading and a standard fixed-bed finishing reactor to complete the alkylation. The first commercial plant began operation in 1994.

#### *Fina/United Catalysts*

This is a new process with an improved catalyst.

### Process Kinetics

As is the case with other zeolite catalyst processes, product selectivity is significantly influenced by the macroporous structure of the zeolite used. As an example, ZSM-5, (medium pore size) favors the primary alkylation reactions, whereas beta-zeolite (large pore size) favors secondary alkylation reactions.<sup>37</sup> For the medium-pore zeolite, the rate expression of choice is based on a Langmuir–Hinshellwood mechanism.<sup>37</sup>

$$r_A = \frac{k_s C_A K_A C_B K_B}{(1 + C_A K_A + C_B K_B)^2}$$

where  $k_A$  = surface reaction rate constant, mol g cat<sup>-1</sup> s<sup>-1</sup>

$C_A$  = concentration of ethylene, moles, L<sup>-1</sup>

$C_B$  = concentration of benzene, moles, L<sup>-1</sup>

$K_A$  = adsorption constant of ethylene, mol<sup>-1</sup>L

$K_B$  = adsorption constant of benzene, mol<sup>-1</sup>L

$r_A$  = rate of alkylation, moles g cat<sup>-1</sup>s<sup>-1</sup>

At a high ratio of ethylene-to-benzene in the feed, the equation was found to simplify to the following:<sup>37</sup>

$$r_A = \frac{A_1 C_B}{(A_2 + C_B K_B)^2}$$

where  $A_1$  and  $A_2$  are constants.

Actual practice employs a significant excess of benzene, for which case the following equation might apply:

$$r_A = \frac{A_1' C_A}{(A_2' + K_A C_A)^2}$$

A further simplification using stoichiometric rate equations has been proposed and may be helpful in any effort to model both the main reaction and side reactions.<sup>38</sup>

$$r_1 = k_1(P_B P_E - P_{EB}/K_1)$$

$$r_2 = k_2(P_{EB} P_E - P_{DEB}/K_2)$$

$$r_3 = k_3 P_E$$

where

$P$  = partial pressure

B, E, EB, DEB = benzene, ethylene, ethylbenzene, and diethylbenzene

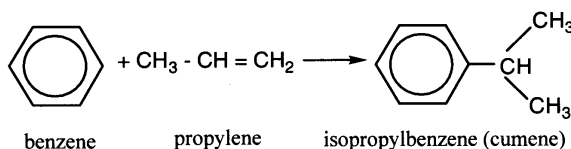
$r_1, r_3, r_3$  = rate of formation of EB, DEB, and side reaction of ethylene, respectively

It is important to consider mass transfer in the commercial scale reaction system, especially for liquid phase operation. This issue is most easily accounted for by an effectiveness factor and a liquid-solid mass-transfer coefficient.<sup>39</sup>

### 2.2.2 BENZENE + PROPYLENE $\rightarrow$ CUMENE (ISOPROPYLBENZENE)

Cumene is used almost exclusively for production of phenol by the Hock process, which was discovered in 1944 and commercialized in 1953.<sup>4</sup> Cumene is oxidized to cumene hydroperoxide which is then converted under acidic conditions to one mole each of cumene and acetone. As with other alkylations, acid-catalyzed processes are used to produce the cumene.

#### Chemistry



Temp., K	$\Delta H$ , kcal	$K_p$
400	23.58	$19.364 \times 10^4$
500	23.14	$5.297 \times 10^2$

#### Operating Conditions (see also Table 2.1)

Process	Catalyst	Temperature	Pressure
SPA, UOP LLC (vapor phase)	65–70% $H_3PO_4$ on silica	200–260°C	30–40 bar
Q-MAX, UOP LLC	beta zeolite	not reported	
MCM-22, Raytheon E&C/Mobil (liquid phase)	mesoporous zeolite	not reported	

#### Side Reactions

Depending on the process, side reactions occur in varying degrees. Side products such as dipropylbenzene, oligomers, and heavier alkylbenzenes can be separated and used for high-octane stock, although they reduce yield.

#### Mechanism

Refer to Figure 2.1, the mechanism for ethylbenzene. In the case of cumene from propylene and benzene, a secondary cation ( $CH_3CH^+CH_3$ ) is formed by attack at the double bond, which is chemisorbed at the active site. Reaction with the  $\pi$  cloud of benzene occurs, and deprotonation follows, yielding the desorbed cumene product and the restored active surface.<sup>15</sup>

## Catalyst Suppliers and Licensors

See Table 2.1.

## Process Units

The catalysts are proprietary, and the processes are licensed. Limited information exists on catalyst details in the open literature.

### *UOP SPA Process (Solid Phosphoric Acid)*

This process actually was originated in the early 1930s by UOP as a means for oligomerizing olefins to product in the gasoline range (polymer gasoline). The process was called the *catalytic condensation process*. It was discovered that, when phosphoric acid and silica were mixed and heated, a solid catalytic material was produced<sup>3</sup> and proved to be effective. During World War II, the need for high-octane components for aviation fuel was critical, and it was known that cumene was a valuable high-octane constituent for aviation gasoline units. Many existing polymer gasoline catalytic-condensation plants were easily converted to the manufacture of cumene by alkylation of benzene with propylene using the same catalyst. Later, when a new demand for cumene developed because of the successful Hock phenol process, many of these plants continued to be used to produce cumene, and others were constructed. The process continues to be the dominant route to cumene. In the early 1990s, 99% of cumene producers used this process. This dominance is slowly declining, as new zeolite catalyst processes have been introduced.

*Catalyst Deactivation (SPA Process)* The phosphoric acid is no doubt in the form of a crystalline hydrate. With use of the usual operating temperature, water is removed, and the catalyst begins to disintegrate. Thus, an important aspect of the operation is a continuous controlled addition of water. If this operation is done carefully, catalyst life of 6–12 months is realized.<sup>16</sup> Ultimately, the catalyst disintegrates as noted by an increase in pressure drop.

Coke also can form on the catalyst, but catalyst replacement often is necessary before coking becomes a problem.

Propylene feed must be free of ethylene and other olefins so as to avoid troublesome product impurities when alkylated. Nitrogen compounds poison the catalyst and must be removed by washing.<sup>14</sup> Thiophene can be present in benzene and is alkylated to isopropylthiophene, which has a boiling point close to cumene. Its presence in cumene feed to the phenol process is detrimental, and it must be removed by mineral-acid washing if present in quantities greater than 0.15%.<sup>14</sup>

*Reactors and Separation Section (SPA Process)* The reactor consists of four adiabatic beds with means for introducing water between beds for both cold-shot cooling and for rehydrating the catalyst.<sup>14</sup> A supplementary inert-liquid quenching stream can also be used.

Early in the operation of the Hock process for phenol from cumene, it was discovered that oligomer impurities in the cumene suppressed the rate of cumene oxidation. As in other benzene alkylation processes, excess benzene was used to deter the side reactions. However, other means were needed to reduce oligomer formation. In the early 1950s, the reactors were designed for upflow with the addition of an inert dispersant in the propylene-benzene feed.<sup>14</sup> Since the exothermic reaction results in temperature increase in the direction of flow, upflow reduces backmixing and reduces the rate of oligomerization.

The feed propylene may contain propane and some other lighter saturated hydrocarbons, but other olefins must not be present, since they will alkylate benzene and produce unwanted alkyl-benzenes. The separation section following the reactor consists of a flash and rectifying system that removes propane and other light ends. The propane is of good quality for commercial fuel use. A significant amount of excess benzene for recycle is separated via the flash system. The enriched cumene is fed to the benzene column, where the remainder of the benzene is recovered. The cumene

from the bottoms is clay treated to remove unwanted heavy hydrocarbons. The clay-treated effluent is then fractionated in a rerun column to separate additional impurities which are close boilers to cumene, and an energy intensive separation is required.<sup>16</sup> The heavies removed can be used as fuel.

The SAP catalyst does not catalyze transalkylation, but a yield of 94–96 wt% is achieved. Many of these plants have a separate transalkylator, which enables a yield of 97–98%.<sup>1</sup> The transalkylator uses a mixed metallic oxide catalyst on silica<sup>14</sup> to convert the ~3% of diisopropylbenzene to cumene.

#### *UOP Q-MAX Process<sup>6,3</sup>*

The Q-MAX process is a relatively new liquid-phase process (1992), with the first plant operational in 1996. A new proprietary zeolite catalyst is used, which is thought to be a beta zeolite. The same catalyst is used for the transalkylation step. Two down-flow reactors in series are used each with two adiabatic beds in series. Propylene is introduced at the inlet of each reactor and between beds. Benzene is fed in modest excess at the inlet of the first reactor.

The separation section is similar to that described for the SAP process, except clay treatment is not required. It consists of a depropanizer, a benzene separation column, and a cumene column, which produces cumene overhead and polysiopropylbenzene (PIB) and heavier aromatics in the bottoms. A final column removes the PIBs (mostly diisopropylbenzenes) overhead and a heavy aromatic fraction, about 1% or less of the overall yield. The overhead is sent to the transalkylator to convert back to cumene. Yields of cumene as high as 99.6 wt% are reported, and cumene purities of 99.97+ wt%.

The catalyst can be regenerated and then only every 18 months. Catalyst life is greater than five years.

#### *Raytheon MCM-22 Process<sup>6,3</sup>*

This liquid-phase process uses a modified Mobil catalyst called MCM-22, similar to that used in the ethylbenzene process. It, as in the companion ethylbenzene process, does not catalyze many of the unwanted side reactions such as oligomerization; excess benzene requirements are modest. The separation section is similar to that described for the Q-MAX process. A product of 99.96% purity is claimed.

#### *Dow/Kellogg 3-DDM Process<sup>6,3,17</sup>*

This liquid-phase process, like the above previous two, permits low excess benzene feed and exhibits low coking tendencies and high yields with small amounts of heavies. The separation section is similar to that described above for the Q-MAX process. Cumene purity of 99.94 wt% minimum is reported.

Interestingly, some information on the catalyst has been reported.<sup>12</sup> The 3-DDM catalyst is said to be a dealuminated mordenite accomplished in a manner to convert the two-dimensional tubular pores to a controlled three-dimensional structure. The resulting shape selectivity favors cumene. Side reactions mainly form p-diisopropylbenzene and a small amount of m-diisopropylbenzene, both of which are transalkylated to form additional cumene.<sup>12</sup> Only a small heavies purge is produced, as is the case with the other zeolite-type processes.

#### *CD Tech Process*

This two-phase process is similar to that described for ethylbenzene.

### **Process Kinetics**

Liquid-phase processes involving proprietary zeolite catalysts have become the most common route to cumene. The alkylation of benzene with isopropylbenzene is a much faster reaction than ethylene alkylation. Mass transfer effects are significant, and the following rate equation combines both mass transfer and reaction, using a simple first-order form for the latter.<sup>39</sup>