

Lecture Ten

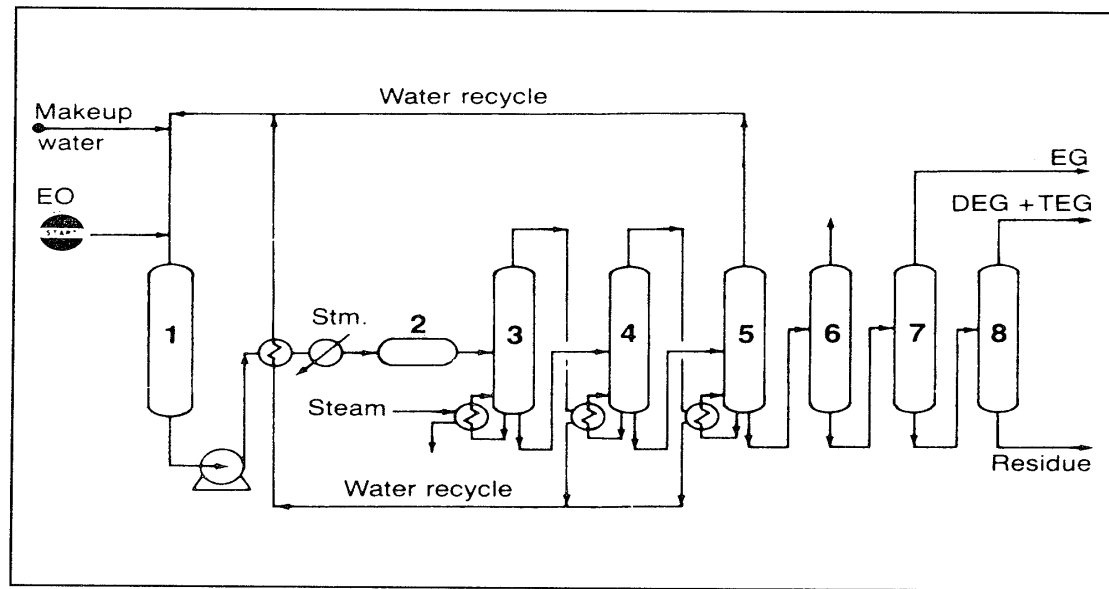
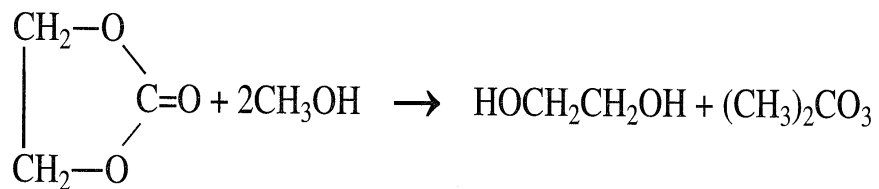


Figure 7-4. The Scientific Design Co. process for producing ethylene glycols from ethylene oxide:(1) feed tank, (2) reactor, (3,4,5) multiple stage evaporators, #4 operates at lower pressure than #3, while #5 operates under vacuum, evaporated water is recycled to feed tank, (6) light ends stripper, (7,8) vacuum distillation columns.

The hydrolysis reaction occurs at a temperature range of 50–100°C. Contact time is approximately 30 minutes. Di- and triethylene glycols are coproducts with the monoglycol. Increasing the water/ethylene oxide ratio and decreasing the contact time decreases the formation of higher glycols. A water/ethylene oxide ratio of 10 is normally used to get approximately 90% yield of the monoglycol. However, the di- and the triglycols are not an economic burden, because of their commercial uses. A new route to ethylene glycol from ethylene oxide via the intermediate formation of ethylene carbonate has recently been developed.

Ethylene carbonate may be formed by the reaction of carbon monoxide, ethylene oxide, and oxygen. Alternatively, it could be obtained by the reaction of phosgene and methanol.

Ethylene carbonate is a reactive chemical. It reacts smoothly with methanol and produces ethylene glycol in addition to dimethyl carbonate:



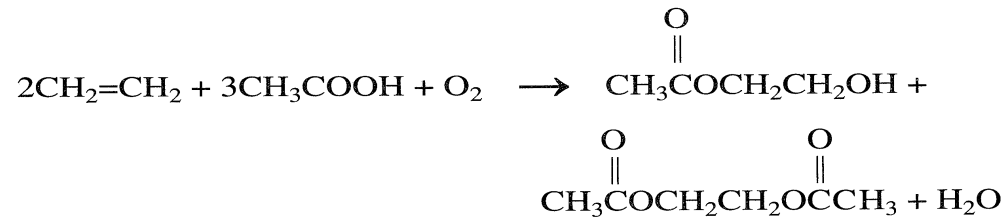
The reaction occurs at approximately 80–130°C using the proper catalyst. Many catalysts have been tried for this reaction, and there is an indication that the best catalyst types are those of the tertiary amine and quaternary ammonium functionalized resins. This route produces ethylene glycol of a high purity and avoids selectivity problems associated with the hydrolysis of ethylene oxide.

The coproduct dimethyl carbonate is a liquid soluble in organic solvents. It is used as a specialty solvent, a methylating agent in organic synthesis, and a monomer for polycarbonate resins. It may also be considered as a gasoline additive due to its high oxygen content and its high octane rating.

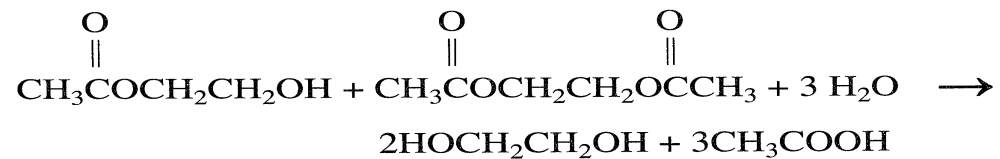
Alternative Routes to Producing Ethylene Glycol

Ethylene glycol could also be obtained directly from ethylene by two methods, the acetoxylation and the oxychlorination processes.

In the acetoxylation process, ethylene is reacted in the liquid phase with acetic acid in the presence of a TeO_2 catalyst at approximately 160° and 28 atmospheres. The product is a mixture of mono- and diacetates of ethylene glycol:

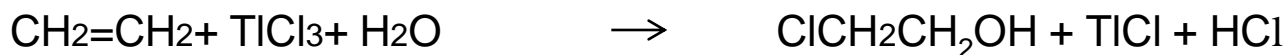


The acetates are then hydrolyzed to ethylene glycol and acetic acid. The hydrolysis reaction occurs at approximately $107\text{--}130^\circ\text{C}$ and 1.2 atmospheres. Acetic acid is then recovered for further use:



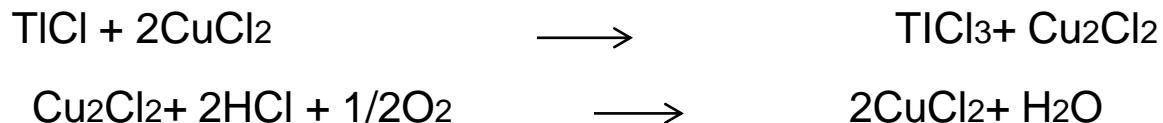
A higher glycol yield (approximately 94%) than from the ethylene oxide process is anticipated. However, there are certain problems inherent in the process such as corrosion caused by acetic acid and the incomplete hydrolysis of the acetates. Also, the separation of the glycol from unhydrolyzed monoacetate is hard to accomplish.

The oxychlorination, on the other hand, is considered a modern version of the obsolete chlorohydrin process for the production of ethylene oxide. In this process, ethylene chlorohydrin is obtained by the catalytic reaction of ethylene with hydrochloric acid in presence of thallium(III) chloride catalyst:



Ethylene chlorohydrin is then hydrolyzed in situ to ethylene glycol.

Catalyst regeneration occurs by the reaction of thallium(I) chloride with copper(II) chloride in the presence of oxygen or air. The formed Cu(I) chloride is reoxidized by the action of oxygen in the presence of HCl:



The overall reaction is represented as:



CHAPTER SIX

Ethane and Higher Paraffins-Based Chemicals

A small portion of vinyl chloride is produced from ethane . In this process a combination of chlorination, oxychlorination, and dehydrochlorination reactions occur in a molten salt reactor. The reaction occurs over a copper oxychloride catalyst at a wide temperature range of 310–640°C. During the reaction, the copper oxychloride is converted to copper(I) and copper(II) chlorides, which are air oxidized to regenerate the catalyst.

Vinyl chloride is an important monomer for polyvinyl chloride (PVC). The main route for obtaining this monomer, however, is via ethylene A new approach to utilize ethane as an inexpensive chemical intermediate is to ammoxidize it to acetonitrile. The reaction takes place in presence of a cobalt-B-zeolite.



However, the process is not yet commercial.

CHAPTER SEVEN

Chemicals Based on Ethylene

INTRODUCTION

Ethylene is sometimes known as the “king of petrochemicals” because more commercial chemicals are produced from ethylene than from any other intermediate. This unique position of ethylene among other hydrocarbon intermediates is due to some favorable properties inherent in the ethylene molecule as well as to technical and economical factors. These could be summarized in the following:

- Simple structure with high reactivity.
- Relatively inexpensive compound.
- Easily produced from any hydrocarbon source through steam cracking and in high yields.
- Less by-products generated from ethylene reactions with other compounds than from other olefins.

Ethylene reacts by addition to many inexpensive reagents such as water, chlorine, hydrogen chloride, and oxygen to produce valuable chemicals. It can be initiated by free radicals or by coordination catalysts to produce polyethylene, the largest-volume thermoplastic polymer. It can also be copolymerized with other olefins producing polymers with improved properties. For example, when ethylene is polymerized with propylene, a thermoplastic elastomer is obtained. Figure 7-1 illustrates the most important chemicals based on ethylene.

Global demand for ethylene is expected to increase from 79 million tons in 1997 to 114 million tons in 2005. In 1998, the U.S. consumption of ethylene was approximately 52 billion pounds.

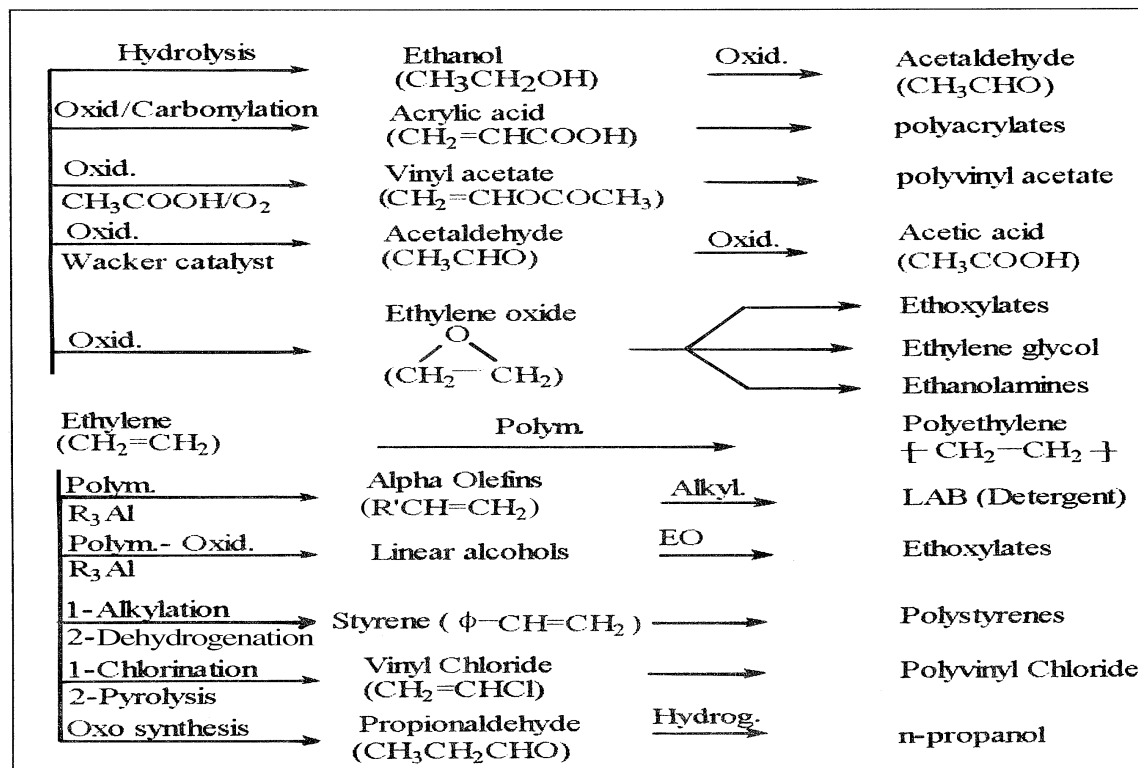


Figure 7-1. Major chemicals based on ethylene

OXIDATION OF ETHYLENE

Ethylene can be oxidized to a variety of useful chemicals. The oxidation products depend primarily on the catalyst used and the reaction conditions.

Ethylene oxide is the most important oxidation product of ethylene. Acetaldehyde and vinyl acetate are also oxidation products obtained from ethylene under special catalytic conditions.

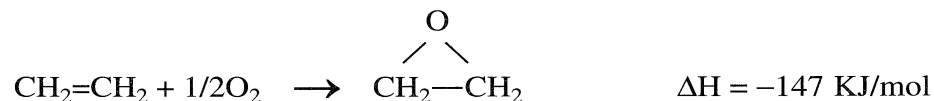


Ethylene oxide (EO) is a colorless gas that liquefies when cooled below 12°C. It is highly soluble in water and in organic solvents.

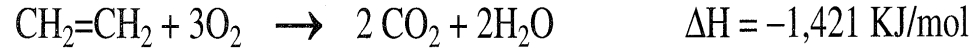
Ethylene oxide is a precursor for many chemicals of great commercial importance, including ethylene glycols, ethanolamines, and alcohol ethoxylates. Ethylene glycol is one of the monomers for polyesters, the most widely-used synthetic fiber polymers. The current US production of EO is approximately 8.1 billion pounds.

Production

The main route to ethylene oxide is oxygen or air oxidation of ethylene over a silver catalyst. The reaction is exothermic; heat control is important:



A concomitant reaction is the complete oxidation of ethylene to carbon dioxide and water:



This reaction is highly exothermic; the excessive temperature increase reduces ethylene oxide yield and causes catalyst deterioration. Over oxidation can be minimized by using modifiers such as organic chlorides.

It seems that silver is a unique epoxidation catalyst for ethylene. All other catalysts are relatively ineffective, and the reaction to ethylene is limited among lower olefins. Propylene and butylenes do not form epoxides through this route.

Using oxygen as the oxidant versus air is currently favored because it is more economical.

In the process (Figure 7-3), compressed oxygen, ethylene, and recycled gas are fed to a multitubular reactor.

The temperature of oxidation is controlled by boiling water in the shell side of the reactor. Effluent gases are cooled and passed to the scrubber where ethylene oxide is absorbed as a dilute aqueous solution. Unreacted gases are recycled. Epoxidation reaction occurs at approximately 200–300°C with a short residence time of one second. A selectivity of 70–75% can be reached for the oxygen based process. Selectivity is the ratio of moles of ethylene oxide produced per mole of ethylene reacted. Ethylene oxide selectivity can be improved when the reaction temperature is lowered and the conversion of ethylene is decreased (higher recycle of unreacted gases).

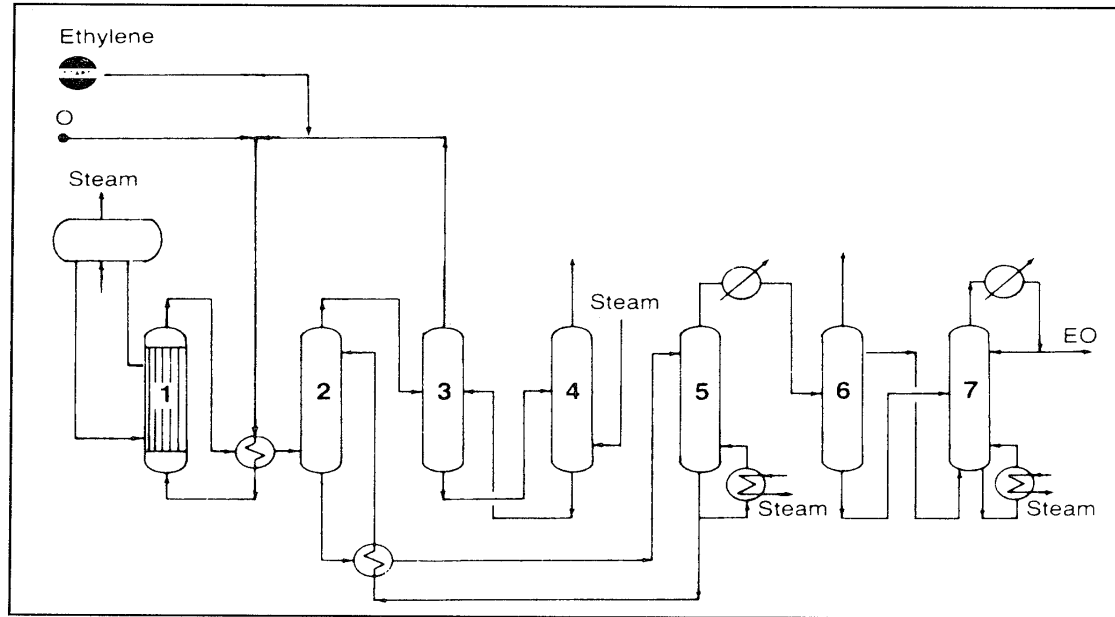


Figure 7-3. The Scientific Design Co. Ethylene Oxide process:(1) reactor, (2) scrubber, (3,4) CO₂ removal, (5) stripper, (6,7) fractionators.

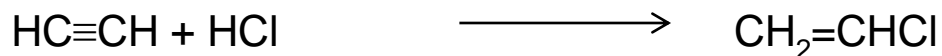
Vinyl Chloride (CH₂=CHCl)

Vinyl chloride is a reactive gas soluble in alcohol but slightly soluble in water. It is the most important vinyl monomer in the polymer industry.

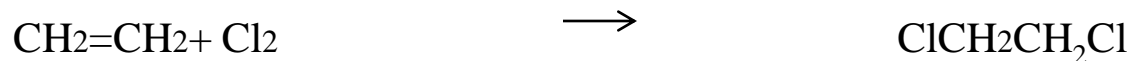
The U.S. production of vinyl chloride, the 16th highest-volume chemical, was approximately 14.8 billion pounds in 1994.

Vinyl chloride monomer (VCM) was originally produced by the reaction of hydrochloric acid and acetylene in the presence of HgCl₂ catalyst.

The reaction is straightforward and proceeds with high conversion (96% on acetylene):

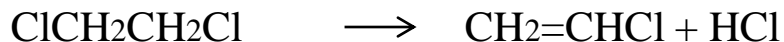


However, ethylene as a cheap raw material has replaced acetylene for obtaining vinyl chloride. The production of vinyl chloride via ethylene is a three-step process. The first step is the direct chlorination of ethylene to produce ethylene dichloride. Either a liquid- or a vapor-phase process is used:

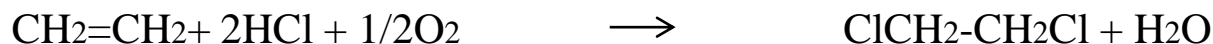


The exothermic reaction occurs at approximately 4 atmospheres and 40–50°C in the presence of FeCl₃, CuCl₂ or SbCl₃ catalysts. Ethylene bromide may also be used as a catalyst.

The second step is the dehydrochlorination of ethylene dichloride (EDC) to vinyl chloride and HCl. The pyrolysis reaction occurs at approximately 500°C and 25 atmospheres in the presence of pumice on charcoal:



The third step, the oxychlorination of ethylene, uses by-product HCl from the previous step to produce more ethylene dichloride:



Ethylene dichloride from this step is combined with that produced from the chlorination of ethylene and introduced to the pyrolysis furnace.

The reaction conditions are approximately 225°C and 2–4 atmospheres.

In practice the three steps, chlorination, oxychlorination, and dehydrochlorination, are integrated in one process so that no chlorine is lost.

Figure 7-5 illustrates the process.

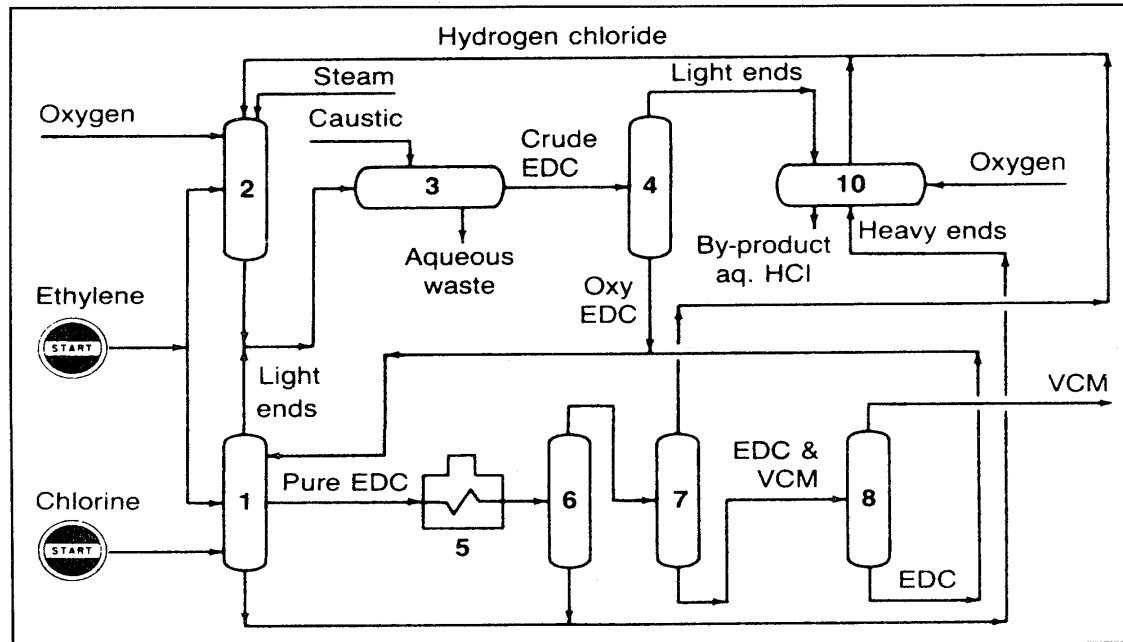
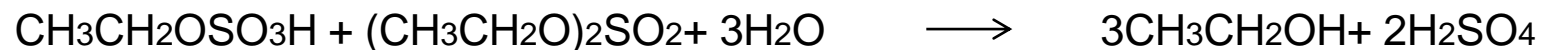


Figure 7-5. The European Vinyls Corporation process for producing vinyl chloride:(1) chlorination section, (2) oxychlorination reactor, (3) steam stripping and caustic treatment of water effluent, (4) EDC distillation, (5) pyrolysis furnace, (6,7,8) VCM and EDC separation, (10) by-product reactor.

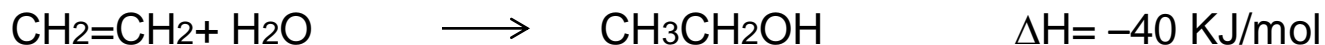
HYDRATION OF ETHYLENE (Ethanol Production)

Ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$) production is considered by many to be the world's oldest profession. Fermenting carbohydrates is still the main route to ethyl alcohol in many countries with abundant sugar and grain sources.

Synthetic ethyl alcohol (known as ethanol to differentiate it from fermentation alcohol) was originally produced by the indirect hydration of ethylene in the presence of concentrated sulfuric acid. The formed mono- and diethyl sulfates are hydrolyzed with water to ethanol and sulfuric acid, which is regenerated:



The direct hydration of ethylene with water is the process currently used:



The hydration reaction is carried out in a reactor at approximately 300°C and 70 atmospheres. The reaction is favored at relatively lower temperatures and higher pressures. Phosphoric acid on diatomaceous earth is the catalyst.

To avoid catalyst losses, a water/ethylene mole ratio less than one is used. Conversion of ethylene is limited to 4–5% under these conditions, and unreacted ethylene is recycled. A high selectivity to ethanol is obtained (95–97%).

Uses of Ethanol

Ethanol's many uses can be conveniently divided into solvent and chemical uses. As a solvent, ethanol dissolves many organic-based materials such as fats, oils, and hydrocarbons. As a chemical intermediate, ethanol is a precursor for acetaldehyde, acetic acid, and diethyl ether, and it is used in the manufacture of glycol ethyl ethers, ethylamines, and many ethyl esters.

OLIGOMERIZATION OF ETHYLENE

The addition of one olefin molecule to a second and to a third, etc. to form a dimer, a trimer, etc. is termed oligomerization. The reaction is normally acid-catalyzed. When propene or butenes are used, the formed compounds are branched because an intermediate carbocation is formed. These compounds were used as alkylating agents for producing benzene alkylates, but the products were non biodegradable.

Oligomerization of ethylene using a Ziegler catalyst produces unbranched alpha olefins in the C_{12} - C_{16} range by an insertion mechanism. A similar reaction using triethylaluminum produces linear alcohols for the production of biodegradable detergents.

Dimerization of ethylene to butene-1 has been developed recently by using a selective titanium-based catalyst. Butene-1 is finding new markets as a comonomer with ethylene in the manufacture of linear low-density polyethylene (LLDPE).