CHAPTER II

THEORETICAL CONSIDERATIONS

2.1 Polystyrene[13]

Polystyrene is a thermoplastic, the designation for polymers that soften when exposed to heat and return to their original condition when cooled to room temperature.

The series of reactions by which liquid styrene is converted into hard, colorless polystyrene has probably been studied. The polymerization reaction of styrene may be represented as shown in figure 2.1 [13].

Figure 2.1 Polymerization reaction of styrene

The overall polymerization is simply the conversion of styrene into polystyrene for which the heat of polymerization is 17.4±0.2 kcal/mole at 26°C.

The two common methods of polymerizing styrene are the batch-suspension process and the mass-continuous technique [14]. The batch-suspension system utilizes a stirred reactor in which the styrene monomer is dispersed in water, with a suspending a agent to maintain dispersion of the monomer droplets in the water phase. Free radical initiators are used to both accelerate the polymerization and to control the molecular weight. The resulting polymer resembles granles of sugar and is washed, dried, and extruded into pellets suitable for use by converters.

Expandable polystyrene is manufactured using the batch suspension system; however, a volatile hydrocarbon blowing agent is added during the polymerization. The expandable polystyrene bead does not undergo the extrusion/pelletization step.

The mass-continuous method pumps styrene monomer through a series of heat exchangers until it is converted to a specified to a specified solids level. The unreacted monomer is then stripped off and recycled to the beginning of the process.

Impact polystyrenes are produced by polymerizing styrene monomer in the presence of an elastomer. Polybutadiene rubber is the preferred elastomer. Block copolymer of styrene-butadiene are sometimes compounded with polystyrene to enhance impact strength.

The suspension technique creates a more versatile product, while mass-continuous results in a more efficient operation. Suspension methods today are usually restricted to specialty products such as expandable polystyrene or to materials which will undergo subsequent compounding such as precolored materials, flame retardant modified grades or color concentrates.

2.1.1 Physical Properties [15]

2.1.1.1 Thermal Properties

Annealed heat distortion is one popular method for measuring the resistance to deformation under heat for polystyrene. This is measured utilizing ASTM method D648. Values from 71°C for super-high-impact grades to 93°C for extrusion-grade crystals are obtainable. The glass transition temperature for unmodified polystyrene is 373 K [15].

2.1.1.2 Toxity

Polystyrene is a low-toxicity product. Almost all commercial available polystyrene are approved by the FDA for food contact applications. The polymer itself is not digestible and is not normally biodegradable [15].

2.1.2 Products

Crystalline polystyrene products, which are transparent, can be infection molded or extruded. Common infection-molded applications include audio equipment dust covers, clear audio tape cassette cases, windows for video cassettes, boxes for compact discs, office supplies, computer disc reels, tumblers, flatware, housewares, display cases, and medical applications such as bottles, petri dishes, and pipettes.

Impact polystyrene injection-molded applications include electronic appliance cabinets, business machine housings, video cassettes, small appliances, smoke detectors, and furniture. Extruded and thermoformed items include refrigerator door liners, luggage, horticultural trays, and some food packaging, such as dairy and yogurt containers.

Extruded non-foamed polystyrene sheet is used in glazing and decorative panels. Oriented polystyrene film and sheet is used in food packaging, such as cookie trays, document wrap, blister pack, and salad containers.

Extruded foam polystyrene is thermoformed into egg cartons, meat and poultry trays, food service trays, and fast food packaging.

Expandable polystyrene is made from polystyrene resin granules impregnated with a blowing agent. After a steamed pre-expansion process that produces foamed beads, the beads are put into a mold again, where they heated with steam and expand further until they fuse together, forming the finished product. The small cellular foam structure gives the material a natural white color. The finished products are used in a wide variety of applications, such as insulation board for the construction industry, molds for metal castings, flotation devices, and packaging materials.

2.1.3 Monomer

Styrene (phenylethylene, vinylbenzene, styrol, cinnamene), $C_6H_5CH{=}CH_2$, is the common name for the simplest and by far the most important member of a group of unsaturated aromatic monomers comprised of variously substituted styrene derivatives. Many different techniques have been investigated for the manufacture of styrene monomer. Of these, the following methods have been used or considered for commercial production [16]:

- Dehydrogenation of ethylbenzene.
- Oxidative conversion of ethlybenzene to α-phenylethanol via acetophenone and subsequent dehydration of the alcohol.
- Side-chain chlorination of ethylbenzene followed by dehydrochlorination.
- Side-chain chlorination of ethylbenzene, hydrolysis to the corresponding alcohols, followed by dehydration.
- Pyrolysis of petroleum and recovery from various petroleum processes.
- Oxidation of ethylbenzene to ethylbenzene hydroperoxide, which is reacted with propylene to give α-phenlyethanol and propylene oxide. The alcohol is then dehydrated to styrene.

2.2 Hydrocracking Reaction and Dual Function Catalyst

Hydrocracking is a catalyst cracking process that takes place in the presence of hydrogen. Cracking of long chain compounds and hydrogenation of the cracked products are the main reactions that take place [17].

The primary process is dehydrogenation of the absorbed paraffin with formation of the corresponding olefin; the secondary process is the addition of a proton from the acid center of the catalyst and formation of a carbonium ion. The ion foamed is either split or isomerised to the thermodynamically mostable tertiary ion. The isomerised ion is again either split or, it transfers the proton to the catalyst. An isoolefin is formed which, on hydrogenation, forms the isomer of the initial substance. The composition of the reaction product will therefore depend on the mutual ratio of reaction rates of the individual processes and, therefore, on the reaction conditions, activity and selectivity of the catalyst employed.

When a sufficiently high temperature is employed or, the hydrogenolytic activity of the catalysts is sufficient intensive, splitting of ions take place in the β-position of the carbonium ion and lower olefins are formed which, on hydrogenation, convert to lower paraffins (or isoparaffins). Alternatively, they are re-protonated and undergo secondary splitting in this form or after preliminary isomerisation . Some alkylation reactions may also take part as side reactions. The hydrocracking rate of n-paraffins differ greatly with lower hydrocarbons.

Dual function catalysts are used in the hydrocracking processes. These catalysts are characterized by providing cracking sites and hydrogenation/dehydrogenation sites. The hydrogenation/dehydrogenation components are usually cobalt, nickel, chromium, tungsten, vanadium or their oxides. These catalysts are usually presulfided before operation and the combination of two or more metals is normal practice.

2.2.1 Preparation and Structure of Dual Function catalyst [18]

The alumina and molecular sieve support are the most frequently used catalysts in isomerization, hydrogenation and dehydrogenation processes. Iron, cobalt, platinum and nickel are the metal of choices because they have activity for the desired reactions without being more than moderately active for undesired reactions such as hydrogenolysis of paraffins. Molecular sieve and alumina supports are the best choices because they are inexpensive, and easily forms the aggregates to maintain a high metal dispersion [18].

One common method of preparing the bifunctional catalysts involves imprgnation of support with an aqueous solution of iron chloride, nickel chloride and cobalt chloride. After impregnation the samples are usually dried and then calcined at temperatures in the range of 450 to 600°C.

2.2.2 Metallic Component [19]

On the metallic component, hydrocarbons can undergo hydrogenation or dehydrogenation reactions in the presence of hydrogen pressure. It is however evident that cobalt and nickel are active catalysts but it is also active in hydrogenation/dehydrogenation reactions. Table 2.1 gives a comparison of the activities of some catalysts in the dehydrogenation of cyclohexane [19].

Table 2.1 Rate of the dehydrogenation of cyclohexane to benzene over different catalysts (temeprature 427°C, Pressure 7 atm) [20]

Catalyst	Dehydrogenation Activity, moles Benzene / g of Catalyst x sec^{-1}
34% Cr_2O_3 on Al_2O_3	0.5
10% Mo_2O_3 on Al_2O_3	3
5% Ni on Al_2O_3	13
5% Co on Al_2O_3	13
0.5% Ir on Al_2O_3	190
1% Pd on Al_2O_3	200
5% Ni on Al_2O_3	320
1% Rh on Al_2O_3	890
0.5% Pt on Al_2O_3	1,400-4,000

2.2.3 Acidic Component

2.2.3.1 Alumina Support

The alumina support used as dual-functional catalysts have been shown to be acidic in nature [21]. The acidic properties are demonstrated by the affinity of these solids for adsorption of basic compounds, such as ammonia, trimethylamine and pyridine. In the case of structure, the aluminium atom is not completely co-ordinated. It is bonded to three oxygen atoms instead of four. The aluminium atom has six valence electrons instead of the maximum eight. It is therefore a Lewis acid and has the potential of accepting a pair of electrons from another species to complete a stable octet. This can be illustrated by the fact that a ammonia which could bond with the aluminium atom in aluminaby donating a pair of electrons to the electron deficient aluminium atom, thus completing a stable octet of electrons Figure 2.2) [22].

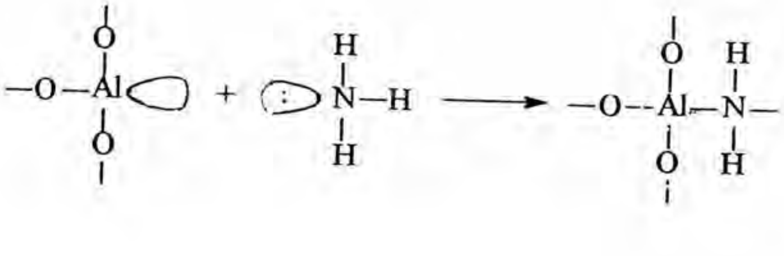

Figure 2.1 Reaction between amonia and aluminium atom

Treatment of alumina with halogens, such as chloride or fluride tends to make the acidic properties of alumina more pronounced, in the sense that it increases the activity of alumina for the catalysis of typical acid catalyzed reaction, such as the skeletal isomerization and various cracking reactions of hydrocarbons.

2.2.3.2 Molecular Sieve

Most industrial applications of molecular sieve are based upon technology adapted from the acid silica/alumina catalysts originally developed for the cracking reaction [23].

This means that the activity required is based upon the production of Bronsted sites arising from the creation hydroxyls within the molecular sieve pore which size is 4 Å. These hydroxyls are usually formed either by ammonium or polyvalent cation exchange followed by calcination step:-

- Ammonium ion exchange

$$\mathrm{NaZ\ (s) + NH_4^+\ (aq) \rightleftharpoons NH_4Z\ (s) + Na^+\ (aq)}$$

$$\mathrm{NH_4Z\ (s) \xrightarrow{calcine} MOH^{(n-1)}\ (s) + HZ\ (s)}$$

- Polyvalent ion exchange

$$\mathrm{NaZ\ (s) + M(H_2O)^{n+} \rightleftharpoons M(H_2O)^{n+}z\ (s) + nNa^+\ (aq)}$$

$$\mathrm{M(H_2O)^{n+}Z\ (s) \xrightarrow{calcine} MOH^{(n-1)}\ (s) + HZ\ (s)}$$

2.3 Reaction Variables [25]

2.3.1 Temperature

Reactor temperature is the primary means of conversion control. The under normal reactor conditions a 20°F increase in temperature almost doubles the reaction rate but does not affect the conversion level as much because a portion of the reaction rate involves mterial that has already been converted to materials boiling below the product end point [25].

2.3.2 Reactor Pressure

The primary effect of reactor pressure is in its effects on the partial pressures of hydrogen. An increase in total pressure increases the partial pressures of both hydrogen. Conversion increases with increasing hydrogen partial pressure. The hydrogen effect is greater, however, and the net effect of raising total pressure is to increase conversion [25].

However, there are a number of variables which must also be considered such as time and catalyst concentration. They depend on the kind of reaction and plastic.