



CHAPTER I INTRODUCTION

Cyclohexanol has its place in various industrial applications, such as the production of adipic acid, a raw material of nylon 66. It is also used as a solvent for lacquers, shellacs, varnishes, cellulose nitrate and resin solutions. Moreover, the chemical is a starting raw material in the preparation of esters for plasticizers, e.g., dicyclohexyl phthalates.

Cyclohexanol is commercially produced from phenol hydrogenation or air oxidation of cyclohexane. In the former, 80% of phenol is hydrogenated to cyclohexanol and cyclohexanone as a by-product by using a metal-catalyst such as Pd/MgO under mild conditions (Claus *et al.*, 2000). In the latter, cyclohexane is oxidized with air to a mixture of cyclohexanone and cyclohexanol, known as K/A oil, as the major products and by-products are alcohols, aldehydes, and ketones. In the oxidation method, the selectivity is as high as 75-80 %; however, the conversion of cyclohexane is as low as 4-6 % due to the thermodynamic limitation. Furthermore, the by-products treatment is expensive (Davis and Kemp, 1990).

Attempts to obtain high conversion and selectivity have been made through the oxidation under mild conditions. An example is the cyclohexane oxidation using N-hydroxyphthalimide (NHPI) combined with a metal-catalyst such as Co or Mn. This process gives higher cyclohexane conversion (40–50%) and selectivity to K/A oil and adipic acid under mild conditions without toxic by-products (Ishii *et al.*, 1997). Another new technology for the cyclohexanol production is cyclohexene hydration using zeolite with the reactive separation technique, which overcomes the thermodynamic equilibrium of the reaction, resulting in nearly 80% conversion to cyclohexanol and cyclohexane as the by-product (Ishida, 1997). However, because of the slurry characteristic of this process, the catalyst separation becomes a problem.

In order to solve the catalyst separation problem, a zeolite packed-bed reactor was used in this work for the hydration of cyclohexene to cyclohexanol. The main objective of this work was to develop a chromatographic system for the cyclohexene hydration and use it to overcome the thermodynamic limitation and

catalyst separation problem. In addition, effects of different catalysts, ZSM-5 and Amberlyst-15 were also investigated on the hydration.

BACKGROUND AND LITERATURE SURVEY

Background information related to this work is provided in this part. First, processes for cyclohexanol production are reported. The concept of the chromatographic reactor is the next focus. Principle of adsorption and selectivity is also given. After that, details of the catalysts are provided.

Background

1. Cyclohexanol Production

Two widely used processes for the cyclohexanol production are phenol-base and benzene base. The former has been favored in the United States while the latter has been in Japan. The choice of each process depends on prices of benzene and phenol in each region. Generally, in Japan, cyclohexanol is produced by oxidation of cyclohexane, generating large amounts of organic acids as by-products, which require expensive treatment methods. Another disadvantage is its severe operating conditions. Moreover, the conversion and selectivity are only 4-6 % and 75-80 %, respectively. Hence, a water-phase reaction from cyclohexene has been proposed as an alternative (Chin and Lee, 1988).

2. A Chromatographic Reactor

A chromatographic reactor can be defined as “a chromatographic column in which a solute or several solutes are intentionally converted, partially or totally, to products during their residence in the column”. As the apparatus is employed as a reactor and separator, both conversion of the starting material and separation of the components take place in the column. In the chromatographic reactor, a fluid mobile

phase is in constant contact with the stationary phase during its passage along the column. The mobile phase may be a gas or liquid, and; therefore, a distinction between gas chromatographic reactor (GCR) and liquid chromatographic reactor (LCR) can be made. The most common stationary phase is the solid or liquid coating on solid support phases. Heterogeneous reactions can be catalyzed by the adsorbent itself or by an additional catalyst that is mixed with the adsorbent. Chromatographic reactors are used for analytical and preparative applications such as reaction kinetic determination, interaction between the stationary and mobile phase examination and characterization of the stationary phase. In addition, chromatographic reactors are employed for the production of chemicals and the preparation of unstable reagents for laboratory use. The use of chromatographic reactors is especially attractive where a chromatographic separation has already been used for purification of the products. The integration of reaction and chromatographic separation offers various advantages. For reversible reactions, conversion can be increased beyond chemical equilibrium by continuously removing the products from the reaction zone. Combination of two unit operations in one apparatus leads to smaller capital expenditure. Although chromatographic reactors offer various advantages, no commercial application on the preparative scale is known so far (Frick and Traub, 2001).

3. Adsorption

Consider a heterogeneous system composed a fluid phase (liquid or gaseous) and a solid surface. Further assume that the fluid phase is a solution of several different chemical species and that the fluid and solid phase are under thermodynamic equilibrium. A species present in the fluid phase is said to be adsorbed on the solid surface if the concentration of the species in the fluid-solid boundary region is higher than that in the bulk of the fluid. Adsorption takes place because of the interaction between the species present in the fluid phase and solid surface.

It is obvious that adsorption is a surface phenomenon and that its definition rests upon concentration measurements and carries no implications of the

mechanism. The species that is adsorbed is called adsorbate. There may be one or more adsorbates in a given adsorption situation. Adsorption-based separation processes, which are developed to separate or purify homogeneous mixture, operate on the principle of difference in adsorption potential and the principle of the extraction in a chromatographic reactor (Ruthven, 1984).

4. Selectivity

The selectivity may vary with differences in either adsorption kinetics or adsorption equilibrium. The separation factor is defined as

$$\alpha_{AB} = \frac{X_A/X_B}{Y_A/Y_B} \quad (2.1)$$

where X_A , X_B , Y_A , and Y_B are, respectively, the mole fraction of component A and B in the adsorbed and fluid phases at equilibrium. The separation factor defined in this way is precisely analogous to the relative volatility, which measures the ease, with which the components may be separated by distillation. However, the analogy is purely formal, and there is no quantitative relationship between the separation factor and relative volatility. For two given components, the relative volatility is fixed while the separation factor varies widely depending on the adsorbent. Because the separation factor generally depends on temperature and often also with composition, the separation factor is a major consideration in the process design. For an ideal Langmuir system, the separation factor is independent on composition and equal to the ratio of the Henry's law constants of the two relevant components. Therefore, preliminary selection of suitable adsorbents can, sometimes, be made directly from available Henry's constants (Ruthven, 1984).

5. Zeolite

In 1756 Cronstedt discovered the naturally occurring minerals, that would one day be known as zeolites. Over the next 150 years, their potential for adsorption/separation science did not come to fruition. Several workers in the early

1800's noted the ability of minerals such as chabazite (a naturally occurring zeolite) to remove odors from air (this is put to great effect still in countries such as Japan). It was not until the early 20th century, due in most part to pioneering work by R.M. Barrer at Imperial College, that zeolite science came of age. The word zeolite is Greek in origin meaning literally Boiling Stone. This was due to the fact that on heating the minerals found by Cronstedt gave off copious amounts of steam. This fact alone opens up zeolites as important materials in adsorption science. The zeolite crystals contain water, and as the water is driven off by heating, there is no discernable collapse of the framework structure. This leads to a highly crystalline, microporous adsorbent, which has an internal structure, which can be easily tailored to adsorb any number of species (Cronstedt, 1756).

Zeolites are crystalline, microporous three-dimensional aluminosilicates, comprised corner-sharing TO_4 tetrahedra ($T = Si, Al$). The general formula is $M_{x/n} [(AlO_2)_x(SiO_2)_y]zH_2O$, where M is an extra-framework cation that balances the anionic charge of the framework. The oxygen atoms are doubly-bridging and connect two metal centers, while the tetrahedra are arranged into n-membered rings, where $n = 4$ or larger. A six-membered ring, for example, contains six "T-atoms" (Si or Al) and six oxygen atoms. For simplification, the latter are ignored in this nomenclature, as well as in structural representations of zeolites, where metal centers are joined by a straight line as shown in Figure 1.

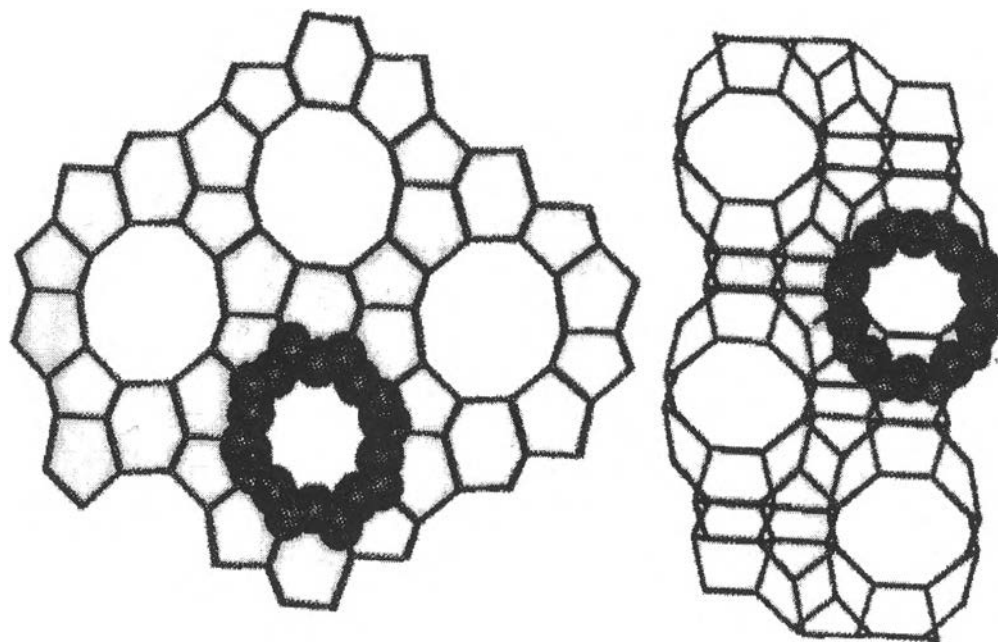


Figure 1 One example of a zeolite open framework (www.chemistry.binghamton.edu).

One example of zeolites is ZSM-5, which contains with two sets of perpendicular, intersecting channels, one defined by 10-membered rings and the other by 8-membered rings. The ZSM-5 structure is a commonly occurring framework topology, where the chemical composition of the metal centers varies. As a result, there are now over 21 different names for this structure, and the material is instead commonly referred to by its assigned three-letter zeolite structure. The specific pore size and shape of zeolites, as well as their high degree of thermal and hydrolytic stability, render them useful for size/shape-selective catalysis (www.chemistry.binghamton.edu).

5.1 ZSM-5

ZSM-5 is a man-made zeolite, which does not occur naturally. It consists of tetrahedral building blocks, in which the central atom is either Si or Al, and the corner atoms are oxygen. Using these tetrahedral building blocks in the same way as molecular lego, the structure of ZSM-5 is produced. On a larger scale, ZSM-5 consists of a 3D channel system. A straight channel system is intersected by a

sinusoidal channel system. The pore diameter is in the order of 5.4 Angstroms. ZSM-5 Zeolites therefore can be seen as the perfect microporous material. They are fairly simple in their synthesis and they can be produced in a number of thermodynamically stable crystalline forms (Cronstedt, 1756).

5.2 Amberlyst-15

Amberlyst-15 is a macroreticular, strongly acidic, polymer catalyst. Its continuous open pore structure makes it an efficient heterogeneous acid catalyst for organic reactions. Amberlyst-15 structure is resistant to breakdown by osmotic, mechanical and thermal shock. It also resists to oxidants such as oxygen and chromate than other polymeric catalysts. Amberlyst-15 can be used directly in aqueous systems or in organic media after conditioning with a water miscible solvent. Amberlyst-15 has the optimal balance of surface area (45 m²/g), acid capacity (H₀, Hammett acidity scale:-2.0) and pore diameter (250 °A) to make it the catalyst of choice for etherification (MTBE, ETBE, TAME), esterification and hydration reaction. Amberlyst-15 wet can also be used for chemical processing applications to remove impurities (metal ions) and basic organic compounds, e.g., amine from aqueous and nonaqueous environments (ROHM and HAAS, 1995).

Literature Survey

Shirafuji and Kavata (1978) and Shirafuji *et al.* (1978a and b) used aromatic sulfonic acids having at least one hydroxyl or ether group as a catalyst in the cyclohexene hydration. In this process, the formed cyclohexanol was separated easily from the reaction solution by extraction and that avoids the cyclohexanol and water azeotropic formation in distillation unit. In this research, p-phenolsulfonic acid, hydroquinonesulfonic acid, cresolsulfonic acid, methoxybenzenesulfonic acid, naphtholsulfonic acid and 3-chro-4-hydroxybenzenesulfonic was used as an aromatic sulfonic acid, having at least one hydroxyl or ether group. p-toluenesulfonic acid, benzenesulfonic acid and naphthalenesulfonic were used as the aromatic sulfonic acid. The results showed that the range of the cyclohexene conversion was 25 to 33

% for the aromatic sulfonic acid having at least one hydroxyl or ether group and was 27 to 31 % for aromatic sulfonic acid. And the percent extraction of cyclohexanol in benzene, using as a solvent, was 68 to 81 % for the aromatic sulfonic acid having at least one hydroxyl or ether group and was 21 to 38 % for aromatic sulfonic acid. According to the results, the cyclohexene hydration by using aromatic sulfonic acid having at least one hydroxyl or ether group as a catalyst, almost the same reactivity as in the aromatic sulfonic acid method was obtained. Moreover, the percent extraction of cyclohexanol from the reaction solution was greatly improved by using the aromatic sulfonic acid having at least one hydroxyl or ether group.

In 1994, Mitsui *et al.* (1994) reported that the cyclohexene hydration with a homogeneous catalyst like sulfuric acid may not be suitable because the product, cyclohexanol, is mostly distributed in the aqueous phase. And that is difficult to separate from other products. Other problems of this system are the equipment corrosion by the acid catalyst and difficulty in maintaining the reaction stability. Consequently, a heterogeneous catalyst with strong acid strength and high thermal stability like ZSM-5 has gained more attention. Mordenite and ZSM-12, both having 12-membered ring pores, produce a large amount of dicyclohexyl ether as a by-product. ZSM-5 and ZSM-11 have an extremely high selectivity (99%) for cyclohexanol because of the shape selectivity of the catalyst. ZSM-5 and ZSM-11 are only zeolites with a high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio and 10-membered ring pores with a three-dimensional structure, which is advantageous for diffusion. However, ZSM-5 is easier in the synthesis than ZSM-11, so it has been applied commercially. Nevertheless, the cyclohexene conversion with ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio 25 and 30) and ZSM-11 are still quite low. And, cyclohexene that is used as a reactant for the hydration process is expensive.

Kucera *et al.* (1995) studied the liquid phase hydration of cyclohexene over faujasite, mordenite and ZSM-5, catalysts at 10 MPa and 150-210 °C in a batch system. Effects of types and Si/Al ratios of the zeolites on the conversion of cyclohexene and the selectivity to cyclohexanol were investigated. The results are in contrast to those of the Mitsui *et al.* (1994). Kucera *et al.* (1995) reported that mordenite with the 70 Si/Al ratio provided the better cyclohexene conversion than

ZSM-5 and faujasite. The selectivity to cyclohexanol was 99% with 27 % of cyclohexene conversion at 200 °C after 4 h.

Fukuoka *et al.* (1997) has developed technology for highly selective partial hydrogenation from benzene by using metallic ruthenium, prepared by a unique preparation procedure. The metallic ruthenium is obtained by reducing a ruthenium compound, which contains a zinc compound and the catalyst consists of primary particles with an average crystalline particle diameter of 200 °A or less. The catalyst has two advantages that are, the inherent instability of the particles (for example, in sintering) is mild and the reaction environment is properly treated. However, other compounds were also examined as co-catalyst candidates, but it was found that the zinc compound exhibited a selectively enhancing effect in the combination with the ruthenium catalyst. The reaction comprises four phases of vapor, oil, aqueous and solid. The catalyst is used in the aqueous phase, and the reactants (benzene and hydrogen) are dissolved in the aqueous phase where the reaction proceeds. Therefore, the products and reactants transfer between the four phases through dissolution, diffusion and extraction, rendering quick transfer a very important factor in the enhancing reaction selectivity. The elevation of the temperature increases the solubility of benzene and hydrogen to the aqueous phase. Reaction temperature of 100 to 180 °C and reaction pressure of 30 to 100 atm are the preferable reaction condition. From the results, up to 60% cyclohexene yield and 70 % of cyclohexene selectivity have been reported, so the process can be succeeded in the commercialization of a new production process for producing cyclohexanol from benzene through cyclohexene.

In 1997, Ishida improved the conversion of the hydration cyclohexene by using the reactive separation technique to overcome the thermodynamic equilibrium of the reaction. ZSM-5 was adopted as the catalyst for this process. It was also reported that while the activity increased with the decrease of the crystal size to 0.5 μm , it did not depend on the size with the size below 0.5 μm . This is probably because all acid sites were effectively used below 0.5 μm . And a large crystal size was deactivated much faster than a smaller crystal size. The work also shows that the activity was directly proportional to acidity. Cyclohexene and cyclohexanol are

very slightly soluble in the aqueous phase. Even though nearly 80 % cyclohexene conversion and 99% selectivity were achieved, the major problem of this process is the catalyst separation from the slurry solution in the batch reactor.

Kulprathipanja and Rekoske (1998) reported that the thermodynamic limitation of the cyclohexene hydration and the catalyst separation were overcome by using a chromatographic reactor. The experiment was performed in 60 cm³ chromatographic reactor by using ZSM-5, ZSM-5 coated spheres and Amberlyst-15 as a catalyst. These results showed that with ZSM-5 or Amberlyst-15 as a catalyst the cyclohexene conversion was obtained up to 95 %. In addition, only cyclohexanol was observed. In other words, the selectivity of cyclohexanol was nearly 100 %. However, the concentration of the outlet cyclohexanol was low.

Akiya and Savage (2000) examined the cyclohexanol dehydration in water at the temperature of 250, 275, 300, 350 and 380 °C with water density ranging from 0.08 to 0.81 g/cm³. Under these conditions, cyclohexanol dehydrated in the absence of catalysts to form cyclohexene as the major product. The most abundant minor products are 1- and 3- methyl cyclopentenes. At the low density of water, the reaction was slow, but the selectivity of cyclohexene was nearly 100%. On other hand, at the high water density, the cyclohexanol conversion was nearly 100 % and methyl cyclopentenes was the by- product.