CHAPTER II
BACKGROUND AND LITERATURE REVEIW

2.1 Overview of Diesel Fuel

Diesel fuel is one of the major fuels used in the world. Diesel fuel is usually used in the on-road diesel engines of trucks, buses and cars and the off-road diesel engines that include locomotives, marine vessels and heavy-duty equipment. The products from crude oil distillation unit, light and heavy gas oil, and FCC unit, straight run gas oil and light cyclic oil (LCO), are the main sources of the diesel fuel. Diesel engine is considerably more fuel-efficient than gasoline engine because they operate at higher compression ratios. Furthermore, more durable and wider power ranges used are added to the advantages of diesel engine.

However, diesel exhaust is relatively not environmental friendly. Diesel exhaust is composed of two phases; either gas or particle and both phases contribute to the risk. The gas phase is composed of many of the urban hazardous air pollutants, such as acetaldehyde, acrolein, benzene, 1,3-butadiene, formaldehyde and polycyclic aromatic hydrocarbons. The particle phase also has many different types of particles that can be classified by size or composition. The sizes of diesel particulates that are of greatest health concern are those that are in the categories of fine and ultra fine particles. The composition of these fine and ultra fine particles may be composed of elemental carbon with adsorbed compounds such as organic compounds, sulfate, nitrate, metals and other trace elements. The small particles that come from diesel exhaust are particularly dangerous because they are coated with a mixture of chemicals such as polycyclic aromatic hydrocarbons, nitroaromatics, benzene, dioxins, and other toxicants. The particles act like a special delivery system that places these toxic chemicals deep within our bodies. Diesel exhaust is like a perversion of a drug delivery system that delivers hazardous toxicants into our lungs. The particles are retained in the body along with the toxic chemical hitchhikers that would otherwise be quickly eliminated. Thus, the particles lengthen our exposures to the toxicants in diesel exhaust.

To reduce the harmful of diesel exhaust, the amount of particle matters can be reduced by decreasing the sulfur contents of the fuel, raising the cetane number, and decreasing the aromatics contents. The latter two are interconnected because reducing the content of aromatics increases the cetane number.

2.2 Hydrogenation of Aromatics Compounds

To achieve deep aromatics hydrogenation, two different methods, that is, single-stage and two-stage hydrotreating processes have been proposed. The single-stage hydrotreating process using conventional hydrotreating catalysts (CoMo, NiMo, and NiW on Al_2O_3) can only work under severe operating conditions, such as much higher hydrogen pressure and higher temperature. However, because aromatic hydrogenation is an exothermic reaction, there are thermodynamic equilibrium limitations at high temperature operation. On the other hand, the two-stage hydrotreating process using metal catalysts in the second stage can achieve deep levels of aromatics hydrogenation under mild conditions, such as moderate hydrogen pressure and lower temperature. However, because metal catalysts are easily poisoned by small amounts of sulfur, the hydrodesulfurization catalyst in the first-stage reactor has to reduce the level of sulfur up to a few ppm. In addition, the effects of sulfur poisoning on the tetralin hydogenation over γ-alumina-supported Pt catalyst were studied by Chang and Chang (1998). The reaction order decreased with severe sulfur poisoning. Therefore, extensive studies have been performed to develop sulfur-tolerant noble metal catalysts for the two-stage process by various petroleum and catalyst manufacturing companies.

In particular, zeolite-supported noble metal catalysts have been receiving more attention as aromatics hydrogenation catalysts. Fujikawa *et al.* (2001) suggested that the lower apparent activation energy for the hydrogenation of aromatics over Pt/HY catalyst is probably responsible for a stronger adsorption of the aromatics on the Bronsted acid sites of the HY zeolite. They concluded that the acidic properties of the catalyst play an important role in the kinetic behavior of aromatics hydrogenation. However, zeolites drastically increase undesirable

cracking activity, which accelerates the rate of coke deposition and enhances the yields of naphtha and gas. These circumstances are caused by too high acidity of zeolite. In 2002, Arribas and co-workers found that the presence of Bronsted acid sites is required to achieve some reactions, for example, isomerization, ring opening, cracking and dealkylation. Furthermore, because zeolite is somewhat expensive, the use of zeolites as a support is economically less attractive.

Noble metal catalysts using for aromatics hydrogenation are usually activated at relatively severe conditions, but nickel catalyst can be operated at mild conditions compared to the other noble catalysts (Rautanen *et al.*, 2002). Moreover, nickel catalyst is cheaper than the others such as platinum and palladium. Therefore, nickel catalyst is considered as an attractive catalyst for hydrogenation of aromatics.

2.3 Steps in a Catalytic Reaction

The overall process by which heterogeneous catalytic reactions proceed can be broken down into the sequence of following individual steps as schematically illustrated in Figure 2.1.

1) Mass transfer (diffusion) of the reactants from the bulk fluid to the external surface of the catalyst pellet.

2) Diffusion of the reactant from the pore mouth through the catalyst pores to the immediate vicinity of the internal catalytic surface.

3) Adsorption of reactant A onto the catalyst surface.

4) Reaction on the surface of the catalyst.

5) Desorption of the products from the surface.

6) Diffusion of the products from the interior of the pellet to the pore mouth at the external surface.

7) Mass transfer of the products from the external pellet surface to the bulk fluid.
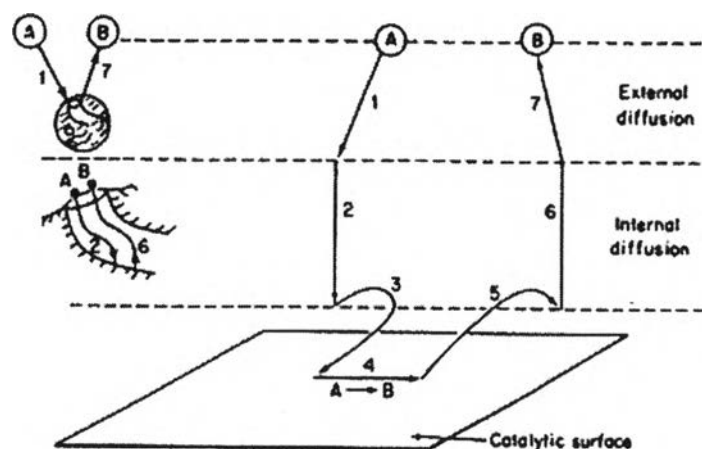
Figure 2.1 Steps in a heterogeneous catalyst reaction (Fogler, 1992).

The overall rate of reaction is equal to the rate of the slowest step in the mechanism. When the diffusion steps (1,2,6 and 7) are very fast compared with the reaction steps (3,4 and 5), the concentrations in the immediate vicinity of the active sites are indistinguishable from those in the bulk fluid. In this situation, the transport or diffusion steps do not affect the overall rate of the reaction. In other situations, if the reaction steps are very fast compared with the diffusion step, mass transport does affect the reaction. In system where diffusion from the bulk gas or liquid to the catalyst surface or to the mouths of catalyst pores affects the rate, changing the flow conditions past the catalyst should change the overall reaction rate. In porous catalysts, on the other hand, diffusion within the catalyst pores may limit the rate of reaction. Under these circumstances, the overall rate will be unaffected by external flow conditions even though diffusion affects the overall reaction rate. Sometimes, two reactants are necessary for a reaction to occur, and both of these may undergo the steps listed above. Other reactions between two substances have only one of them adsorbed.

2.4 Adsorption (Satterfield, 1991)

For a catalytic reaction to occur, at least one and frequently all of the reactants must become attached to the surface. This attachment is known as adsorption and takes place by two different processes: physical adsorption and

chemisorption. Physical adsorption is similar to condensation. The process is exothermic, and the heat of adsorption is relatively small, being one the order of 1 to 15 kcal/g mol. The forces of attraction between the gas molecules and the solid surface are weak. These van der Waals forces consist of interaction between permanent dipoles, between a permanent dipole and induced dipole, and/or between neutral atoms and molecules. The amount of gas physically adsorbed decreases rapidly with increasing temperature, and above its critical temperature only very small amounts of a substance are physically adsorbed.

The type of adsorption that affects the rate of a chemical reaction is chemisorption. Here, the adsorbed atoms or molecules are held to the surface by valence forces of the same type as those that occur between bonded atoms in molecules. Like physical adsorption, chemisorption is an exothermic process, but the heats of adsorption are generally of the same magnitude as the heat of a chemical reaction. If a catalytic reaction involves chemisorption, it must be carried out within the temperature range where chemisorption of the reactants is appreciable.

2.5 Kinetic Models (Satterfield, 1991)

2.5.1 Langmuir-Hinshelwood Model

The assumptions underlying the Langmuir adsorption isotherm are retained. Further, adsorption equilibrium is assumed to be established at all times; for example, the rate of reaction is taken to be much less than the potential rate of adsorption or desorption. The concentrations of adsorbed species are therefore determined by adsorption equilibrium as given by the Langmuir isotherm. If two or more species are present, they compete with each other for adsorption on a fixed number of active sites. Reaction is assumed to occur between the adsorbed species on the catalyst. If a single reactant is decomposed, the process may be assumed to be either unimolecular or bimolecular, depending on the number of product molecules formed per reactant molecule and whether or not the products are adsorbed. For example, in the case of bimolecular reaction,

$$A + B \longrightarrow C$$

If assumptions made are in the following:

   1. All compounds may be appreciably adsorbed.

   2. The rate of reaction is proportional to the quantity of adsorbed A
and B.

   3. No dissociation of A and B molecules occurs on adsorption.

   4. Reverse reaction is negligible.

The rate of reaction will be expressed as:

$$-r = \frac{kK_A P_A K_B P_B}{(1 + K_A P_A + K_B P_B + K_C P_C)^2} \tag{2.1}$$

where k is the reaction rate constant, K_A and K_B are the adsorption constants of A and B respectively, and P_A, P_B and P_C are the partial pressures of A, B and C.

2.5.2 Rideal Model

The idea was revived in 1939 by Rideal, who proposed that a simple molecular mechanism for heterogeneous catalytic reactions was reaction between a chemisorbed radical or atom and a molecule. The latter impacting directly from the gas phase or held in a deep van der Waals layer. In either case a new chemisorbed species was formed on the surface. Specifically, Eley and Rideal (1941) concluded that the conversion of p-hydrogen to o-hydrogen on tungsten and the exchange of hydrogen and deuterium occurred between a hydrogen molecule in a loosely bound layer and a strongly bound chemisorbed hydrogen atom. However, it now appears that the para-to-otho conversion occurs instead by adsorption of a hydrogen molecule with dissociation, a mechanism proposed by Binhoeffer and Farkas (1931).

Reactions of this general type are referred to variously as Langmuir-Rideal, or Rideal-Eley mechanisms. Only a few reactions have been clearly shown to proceed in this manner. The hydrogenation of ethylene has been intensively studied and the results on some catalysts such as nickel under some conditions are consistent with a Rideal mechanism. On other catalysis such as copper, a Langmur-Hinshelwood mechanism seems more probable.

To formulate the Rideal mechanism for a simple reaction between A and B to form C, retain all the other assumptions in the Langmuir-Hinshelwood model and consider reaction occurring between adsorbed molecules of B and gas-phase molecules of A. The rate is

$$-r = k\theta_B P_A \tag{2.2}$$

where θ_B is the fractional surface coverage of substance B.

Performing the usual substitutions, one obtains

$$-r = \frac{kP_A K_B P_B}{1 + K_A P_A + K_B P_B + K_C P_C} \tag{2.3}$$

If the mechanism were assumed to be reaction between adsorbed A and gas-phase B, an equation of the same form is obtained, but with K_A replacing K_B

$$-r = \frac{kP_B K_A P_A}{1 + K_A P_A + K_B P_B + K_C P_C} \tag{2.4}$$

The mechanism expressed by Eq.(2.2) could occur either with or without significant adsorption of A onto the catalyst surface (Langmuir, 1921), so further information is needed to determine whether or not the term $K_A P_A$ should be included in the denominator of Eq. (2.3).

The rate-limiting step may also be indicated by formulating the kinetic expression for the rate of reaction for each different, plausible rate-limiting step. Each formulation is then compared with experimental data, and the mathematical form that best fits the experimental facts suggests a possible mechanism for the reaction. Frequently the same mathematical form may be derived from more than one different postulated mechanism, in which case the parameters may have considerably different theoretical interpretations. Hence, the fitting of data to a

particular mathematical expression seldom, of itself, proves much concerning the true mechanism. The extent to which these approaches lead to reliable and useful conclusions varies greatly from case to case and calls for astute judgment on the part of the investigator.

Liquid phase tetralin hydrogenation on a nickel catalyst has been studied in 2001 by Rautanen *et al*. They proposed the mechanistic based model that includes competitive adsorption of tetralin and hydrogen and the dissociative adsorption of hydrogen is the best fit.   In 1995, Smeds *et al.* had investigated kinetics of ethylbenzene. They proposed a mechanistic modeling suggested that the reaction rate was governed by three steps of pairwise sequential addition of hydrogen atoms to adsorbed ethylbenzene. Also, they studied the hydrogenation of *o*- and *p*-xylene on Ni/Al_2O_3 and proposed the mechanistic scheme which the pairwise of adsorbed hydrogen are reacted with adsorbed hydrocarbon. However, several omissions and contradictory results among these papers are present. For example, in Rautanen's papers he could not get rid of internal mass transfer limitations. In this study it is presented a different strategy to approach semi empirical kinetic studies, an intermediate between the rigorous microkinetic studies and the mostly math oriented, with very little physical interpretation, kinetic models. It is attempted to give a valuable input in the determination of physically meaningful parameters that can lead to a better understanding of the hydrogenation of tetralin.